

Nuclear Methods in Environmental Science

STUDIES ON ^{226}Ra AND ^{210}Pb ACTIVITIES AND THE CONCENTRATION FACTORS OF ^{226}Ra IN THE SURFACE ORGANIC LAYERS OF THE ESTUARINE SEDIMENTS OF MINDOLA AND PURNA RIVERS IN INDIA

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The sediment samples have been collected from estuarine regions of Mindola and Purna of Gujarat State. These samples are found to contain less than 3% of organic matter which scavenge and carry most of the activity of ^{226}Ra , etc., to the sediment floor. The activities of ^{226}Ra are found to vary from 0.1 to 0.5 pCi/g, while ^{210}Pb activities lie in the range of 3 to 8 pCi/g. These activities find their way into the organisms present in sea water and then into fish which is finally consumed by humans. This paper gives in detail the sampling techniques, experimental procedures and the distribution of the isotopes of ^{226}Ra and ^{210}Pb in the estuarine regions and the concentration factors of ^{226}Ra in the region.

Introduction

The densely populated regions of the world are found in a strip of about 250 miles wide around Pacific, Atlantic and Indian Oceans. The major industrialized cities are situated near the rivers which are navigable to sea. Naturally, man's activities in the ocean will continue to be in the areas close to the coastline particularly in the estuarine regions. The major fraction of naturally occurring and artificially produced radionuclides which find their way into the estuaries will never reach the open sea but will accumulate in the estuaries. These areas are important to fisheries because they serve as nursery areas for larval and immature forms. It has been estimated that more than 65% of fish harvested occupy estuarine areas during some phase of their life cycle. The organisms present in such areas accumulate radionuclides and transport them from

shallow water areas to man. This distribution of radionuclides may not be significant as compared to the total amount of these radionuclides released into marine environment but this will result in the ingestion of undesirable concentrations of the radionuclides by persons consuming large amounts of sea food from limited regions over long periods of time.

Sample collection

The sediment samples were collected from top layers (<15 cm deep) at each location in the estuarine region. In the sampling procedure, a number of sediment samples was collected from nearby places at each sampling station.

These sediments were pooled together and then used as representative sample of the respective stations. Fig. 1 gives the locations of sampling stations of Mindola and Purna estuaries from Gujarat State. The sediment samples were air-dried in aluminium trays.

Experimental procedures

Dissolution of the sediment sample

5 g of the sediment sample is heated with 60 ml of aqua regia. 2 ml of Pb carrier (15 mg of Pb/ml) and 1 ml of Ba carrier (400 μg of Ba/ml) is added and the residue is again heated with 60 ml of aqua regia. The dried mass is treated with 10 ml of concentrated hydrochloric acid and evaporated to dryness. The dried residue is finally dissolved in 200 ml of 1.5N hydrochloric acid.

Radiochemical separation of lead and radium

Ion-exchange columns. The anion-exchange resin, Dowex-1 X 8% (50–100 mesh) is washed with running distilled water to remove the fine particles. 15 g of the resin is then loaded in a pyrex glass column (1 X 45 cm).

Column operations. 1. 150 ml of 1.5N HCl is passed through the column at a flow rate of 1.0 ml/min and the effluent is rejected.

2. The sample containing Pb which was dissolved in 200 ml of 1.5N HCl is passed through the column at a flow rate 0.5 ml/min. The Pb is adsorbed on the column. The effluent is collected in a separate beaker for the separation of radium.

3. The ion-exchange column is washed with 100 ml of 1.5N HCl at a flow rate of 0.5 ml/min and the effluent is collected.

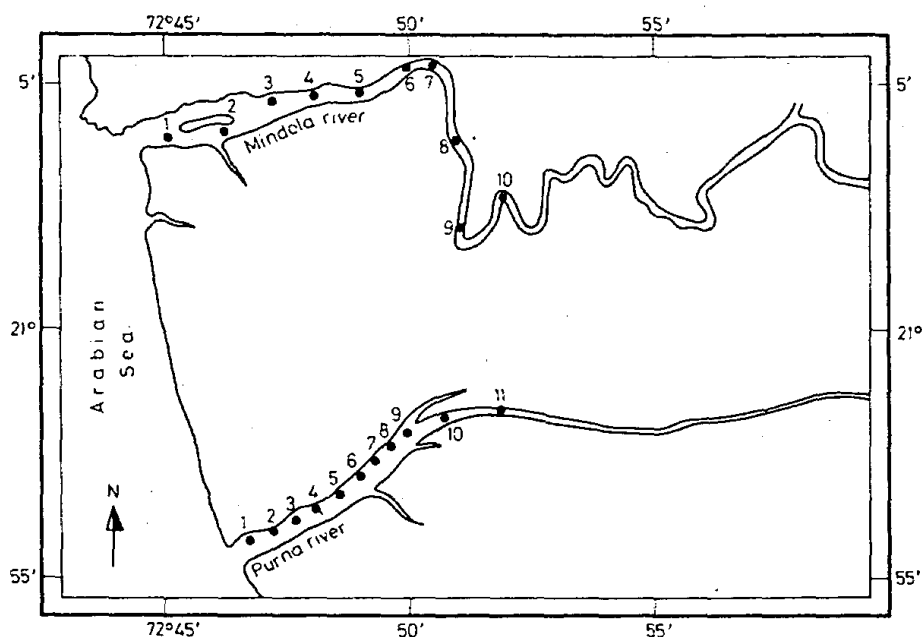


Fig. 1. Location of sampling stations in Mindola and Purna estuarine regions

4. Lead adsorbed on the ion-exchange column is then eluted with 150 ml of de-ionized water at a flow rate of 0.5 ml/min.

Purification of lead

Lead is precipitated as lead sulfate by dropwise addition of concentrated sulfuric acid. The precipitate is allowed to settle down and then filtered through Whatman 542 filter paper. It is then dissolved in 6N ammonium acetate. Lead is precipitated as lead sulfide by bubbling hydrogen sulfide through the solution. The precipitate of lead sulfide is dissolved in concentrated nitric acid and finally lead is precipitated as lead sulfate. Chemically pure lead sulfate precipitate is filtered through Whatman 542 filter paper one inch in diameter. The precipitate is weighed in order to obtain the chemical yield.

Purification of radium

The effluents obtained from steps (2) and (3) of the column operations, are pooled together and evaporated to dryness. The residue is dissolved in dilute nitric acid. A few

drops of 3N citric acid are added to the solution and radium is co-precipitated with barium and lead carriers as sulfate. The precipitate is dissolved in 0.25 M EDTA and radium is finally co-precipitated with barium as sulfate. The precipitate is transferred to a stainless steel disc one inch in diameter and then weighed to determine the chemical yield.

Counting

Betas. The purified lead sulfate samples are kept for one month for the daughter ^{210}Bi to attain equilibrium with ^{210}Pb . These samples are counted in a low background end window Geiger counter. The background of the counter is 0.7 count/min. The counting efficiency is 12.7%. The 1.17 MeV betas of the daughter product ^{210}Bi are counted and the build-up of the activity with a half-life of 5 days is followed for a period of one month in order to check the radiochemical purity. The counting statistics is better than $\pm 5\%$ standard deviation.

Alphas. The precipitate of radium is allowed to age for 72 days in order to allow ^{223}Ra ($T = 11.44$ d) and ^{224}Ra ($T = 3.64$ d) to die down. The stainless steel disc containing precipitate of radium is flamed for one minute to expel radon trapped in the precipitate and then counted in a silicon surface barrier detector (active area 200 mm^2 and a depletion dept of 700μ) coupled to a low noise amplifier, a pre-amplifier and 400 channel analyzer. The counting efficiency of the detector is 24%.¹ The standard deviation obtained for the counts under ^{226}Ra peak lie in 5–7% range.

Results and discussion

Table 1 gives the activities of ^{210}Pb , ^{226}Ra and the activity ratios of $^{210}\text{Pb}/^{226}\text{Ra}$ in sediment samples of Mindola estuary. ^{210}Pb activity is found to lie in the range of 3 to 8 pCi/g, while ^{226}Ra activity is found to vary from 0.1 to 0.5 pCi/g. However, there is a large variation of the activity ratios of $^{210}\text{Pb}/^{226}\text{Ra}$ from 15.8 to 30.0.

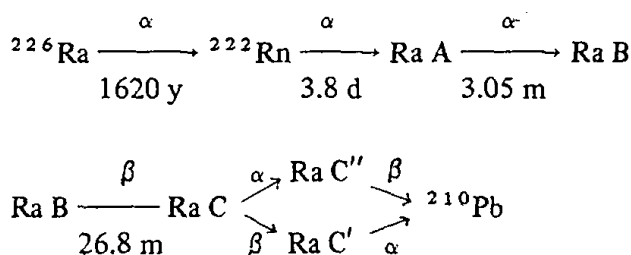
Mindola river is narrow in fresh water region and broadens appreciably in the mouth region. The course of this river through south Gujarat State of India is in east-west direction till it meets the Arabian Sea. The rapid industrialization of Surat city and neighbouring regions has resulted in disposal of wastes from various industries into Mindola river either directly or through creeks which join the river in estuarine and fresh water areas. Currents are very strong in the estuarine region which disperse the bottom sediment in the water column resulting in a high and variable suspended load (10–1000 mg/l). Because of the presence of this high concentration of suspended

Table 1
Activities of ^{210}Pb , ^{226}Ra and activity ratio of $^{210}\text{Pb}/^{226}\text{Ra}$ in sediment samples of Mindola estuary

Sampling location	^{210}Pb pCi/g	^{226}Ra pCi/g	Activity ratio $^{210}\text{Pb}/^{226}\text{Ra}$
Mindola (1)	3.0	0.1	30.0
Mindola (2)	4.6	0.2	23.0
Mindola (3)	3.5	0.2	17.5
Mindola (4)	4.6	0.2	23.0
Mindola (5)	7.9	0.5	15.8
Mindola (6)	8.0	0.3	26.7
Mindola (7)	7.8	0.4	19.5
Mindola (8)	7.6	0.4	19.0
Mindola (9)	7.9	0.3	26.3
Mindola (10)	8.0	0.3	26.7

particles, the radio-nuclides such as ^{210}Pb , ^{226}Ra , etc. present in estuarine and river waters are scavenged by the suspended particles and are finally deposited on the floor of the estuarine regions.

The radioisotopes ^{226}Ra and ^{210}Pb are intermediate members of the ^{238}U decay series, a part of which is given below:



Since ^{226}Ra and ^{210}Pb are the members of the same uranium series, both the radioactive isotopes should have been in equilibrium. But from the results of measurements of the activities of ^{226}Ra and ^{210}Pb , it is observed that these isotopes do exhibit anomalous behaviour. This may be explained on the basis of preferential leaching of the isotope of radium. Radium being more water soluble, it is found to move faster than Pb.

Table 2 gives the activities of ^{226}Ra , ^{210}Pb and the activity ratios of $^{210}\text{Pb}/^{226}\text{Ra}$ in sediment samples collected from Purna estuary. The activity of ^{226}Ra is in the range

Table 2
Activities of ^{210}Pb , ^{226}Ra and activity ratios of
 $^{210}\text{Pb}/^{226}\text{Ra}$ in sediment samples of Purna estuary

Sampling location	^{210}Pb pCi/g	^{226}Ra pCi/g	Activity ratio $^{210}\text{Pb}/^{226}\text{Ra}$
Purna (1)	3.1	0.1	31.0
Purna (2)	5.0	0.2	25.0
Purna (3)	4.5	0.2	22.5
Purna (4)	6.3	0.5	12.6
Purna (5)	5.0	0.2	25.0
Purna (6)	4.9	0.2	24.5
Purna (7)	6.2	0.4	15.5
Purna (8)	7.9	0.3	26.3
Purna (9)	8.0	0.4	20.0
Purna (10)	7.5	0.3	25.0
Purna (11)	7.8	0.3	26.0

of 0.1 to 0.4 pCi/g, while ^{210}Pb activity lies in the range of 3.1 to 8 pCi/g. However, the activity ratios of $^{210}\text{Pb}/^{226}\text{Ra}$ are found to vary in the range of 15.5 to 31.0. These values of activities of ^{226}Ra and ^{210}Pb are almost close to those obtained for sediment samples collected from Mindola.

*$^{226}\text{Ra/g}$ of the surface organic layer
Particle size determination*

(1) Sediment samples from various locations of Mindola and Purna estuaries are shaken with distilled water for 4 hrs, and then allowed to settle on a 0.22μ membrane filter. The filter paper is dried in air and few drops of emulsion oil are added to the filter paper. The size of the particles and the number frequency are determined microscopically.

(2) The sediment particles are then suspended in distilled water, the pH is adjusted to 9.0 using sodium hydroxide solution and then shaken for 4 hrs. The particle suspension is transferred to 0.22μ membrane filter and to the membrane dried in air a few drops of emulsion oil are added. The size of the particles and the number frequency are then determined microscopically.

(3) The organic matter present on the surface of the sediment particles is destroyed using 0.05N hydrochloric acid and phosphate-free hydrogen peroxide. The sediment

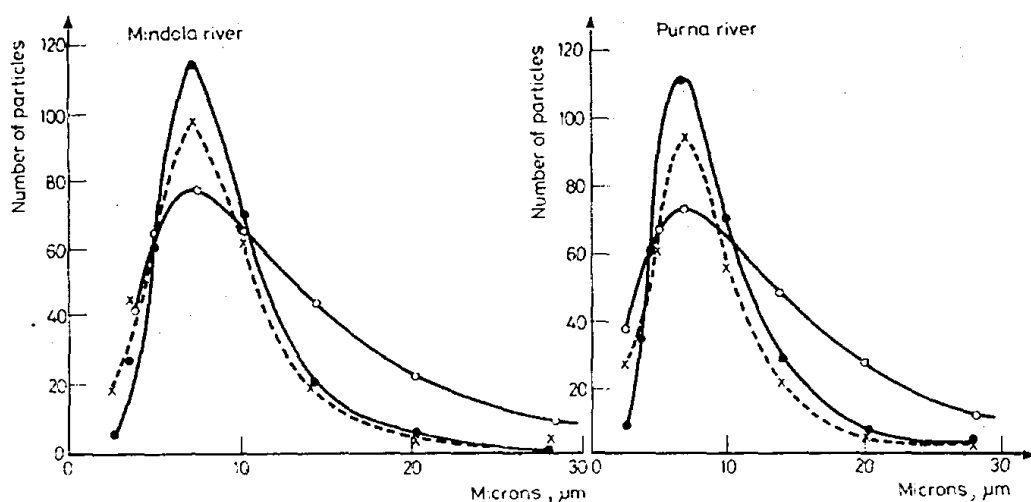


Fig. 2. Particle size distribution for estuarine sediments. Curves: ● – distribution for organic matter destroyed sediment; ○ – distribution for sediment shaken with distilled water; x – distribution for sediment shaken with sodium hydroxide

particles are then washed with 0.05N hydrochloric acid and then with distilled water. The washed sediment particles are suspended in water, the pH is adjusted to 9.0 and the mixture shaken for 4 hrs. The particle suspension is transferred to 0.22 μ membrane filter and a few drops of emulsion oil are added. The size of the particles and number frequency are determined microscopically.²

Fig. 2 gives particle size distribution for estuarine sediments.

Thickness of the surface layer of labile component. From the data of the particle size measurements, the total weight and the total surface area of the particles are calculated. The densities of the sediment particles with and without organic surface layer have been obtained experimentally. From these data, the volume of the surface layer of the labile component is calculated. Using these data, the thickness of the surface layer of the labile component is obtained.³ These values are found to be in the range of $0.4 \cdot 10^{-5}$ cm to $0.9 \cdot 10^{-5}$ cm.

$^{226}\text{Ra/g}$ of the surface organic layer. The surface area per unit weight of the sediment particles is obtained from particle size determinations. The thickness of the surface labile layer of organic matter has been calculated. From these data, the volume of the surface organic layer has been obtained. The weight of the surface organic layer is then calculated from the volume and density of the organic layer. $^{226}\text{Ra/g}$ of the sediment is obtained by surface leaching of the sediment particles with 5% EDTA at pH 8. From the values of ^{226}Ra concentration and the weight of the surface organic layer, $^{226}\text{Ra/g}$ of the surface organic matter is calculated. Table 3 gives the results of the measurements.

Table 3
 $^{226}\text{Ra/g}$ of the surface organic layer

Place of collection	Total Surface area X 10^{-3} cm ² of the particles counted	Total weight X 10^{-6} g of the particles counted	Surface area per gram of the sediment X 10^{-3} cm ²	Thickness of the surface layer X 10^{-5} cm	Volume of the surface organic layer per gram of the sediment X 10^{-3} cm ³	Weight of the surface organic layer per gram of the sediment X 10^{-2} g	$^{226}\text{Ra/g}$ of the sediment (pCi/g)	$^{226}\text{Ra/g}$ of the surface organic layer (pCi/g)
Mindola	0.70	0.33	2.15	0.89	1.90	2.37	0.21	9.0
Purna	0.64	0.27	2.31	0.49	1.13	1.41	0.20	14.0

Concentration factors of ^{226}Ra . The values obtained for ^{226}Ra in waters of the estuaries of Mindola and Purna and the values of ^{226}Ra in the organic layers, the calculated concentration factors range from 18000 to 50000.

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