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DETERMINATION OF NATURAL AND ARTIFICIAL RADIONUCLIDES IN SEA WATER AND SEDIMENTS OFF GWADAR COAST, ARABIAN SEA

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Determination of naturally occurring radionuclides (^{226}Ra, ^{228}Ra, ^{40}K) and fission fragment (^{137}Cs) in shallow sea water and sediment samples collected from Gwadar coast, Pakistan has been carried out. The activity detected in various sediment samples ranged from 16.9±2.1 to 31.7±3.2 Bq.kg^{-1} for ^{226}Ra, 9.8±1.2 to 13.3±1.2 Bq.kg^{-1} for ^{228}Ra and 152.4±11.4 to 244.4±15.7 Bq.kg^{-1} for ^{40}K. In water samples the activity detected for ^{40}K ranged from 9.3±0.8 to 17.5±3.0 Bq.l^{-1}. The levels of radioactivity for Gwadar area have been compared with the results published in literature for other regions of the world i.e., Irish sea sediment (^{226}Ra = 23.9 Bq.kg^{-1}, ^{228}Ra = 36.7 Bq.kg^{-1}), Pacific Ocean sediments, (^{226}Ra = 21.4±1.1 Bq.kg^{-1}), Indian Ocean sediment, (^{226}Ra = 13.8 Bq.kg^{-1}, ^{228}Ra= 26.7 Bq.kg^{-1}, ^{40}K = 297.0 Bq.kg^{-1}) and Bay of Bangal (^{226}Ra = 13.9 to 25.2 Bq.kg^{-1}, ^{40}K = 118.3 to 651.9 Bq.kg^{-1}). The level of ^{40}K for Irish sea water is 11.4 Bq.l^{-1}. The mean values of radium equivalent activity, absorbed dose rate and effective dose are 58 Bq.kg^{-1}, 27 nGy.h^{-1} and 0.03 mSv.y^{-1} respectively. The value of effective dose is much below the level of 1.0 mSv.y^{-1}, for general public based on stochastic effects recommended by International Commission on Radiological Protection (ICRP). As previously no data on radioactivity of coastal environment of Pakistan is available, the data presented here will serve as baseline for radionuclide concentration in seawater and sea sediments of the study area, and will be included in International Atomic Energy Agency, IAEA's, Asia Pacific Marine Radioactivity Database (ASPAMARD).

Keywords: Radionuclides, Gamma spectrometry, Arabian sea, Sea sediments, Sea water

1. Introduction

Natural radionuclides are always present in the earth's crust, whereas a large number of radionuclides are produced artificially during processes like fission, fusion and nuclear activation [1]. Release of low levels of artificial radionuclides can occur to the environment during normal operations of nuclear installations such as nuclear reactors, particle accelerators, production and application of radioisotopes in the fields of nuclear medicine, research, industry and agriculture [2]. Higher quantities of radioactive materials may be introduced into the environment due to atmospheric/underground nuclear weapon testing and accidents at nuclear installations. Naturally occurring radioactive materials are released to the environment during mining and milling of mineral ores, ore processing, uranium enrichment, nuclear fuel fabrication and handling of the fuel cycle end tailings.

Release of radioactive elements into the atmosphere may contaminate ground, water, air and the biological organisms [3,4]. Most of the radioactivity deposited on the surface soils is washed and drained through rivers to the oceans. Part of the ground deposited activity may adsorb on the soils and percolate with the underground waters to oceans, though in the longer times. Among the major marine radioactivity sources are global fallout, radioactivity transfer from other areas by seawater movements and through biota, coastal and inland nuclear power plants, nuclear submarines, radioactive waste dumping operations in the sea. Radionuclides reaching the ocean become part of the marine ecosystem and are found in water, sediments and marine organisms [5,6,7].

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Table 1. Geographical locations and identification codes of marine sediment and water samples collected from selective locations of Gwadar coast.

Sample ID	Sample Location/ Reference Site	Geographical Location	
		Longitude	Latitude
Sediments			
GDS1	Near coast guard East Bay	62.3406E	25.1565N
GDS2	Opposite PIA office East Bay	62.338E	25.1496N
GDS3	Between PIA office and T&T East Bay	62.3347E	25.1419N
GDS4	Opposite T & T exchange East Bay	62.3339E	25.1378N
GDS5	Gwadar fish harbour	62.3348E	25.1217N
GDS6	Near boat making area West Bay	62.3197E	25.1272N
GDS7	Opposite girls school West Bay	62.3352E	25.0911N
GDS8	Opposite governor house West Bay	62.3157E	25.1574N
Seawater			
GDW1	Gwadar Open Sea	62.3287E	25.0889N
GDW2	Boat building area West Bay	62.3200E	25.1284N
GDW3	Opposite Girls School West Bay	62.3174E	25.1363N
GDW4	Opposite PIA office East Bay	62.3406E	25.1514N
GDW5	Opposite T & T Exchange East Bay	62.3420E	25.1127N

Accumulation of radioactive substances in the marine coastal environment causes problems concerning safety of biotic life, and ultimately reaches to humans through food chain. To address these problems assessment of radioactivity concentration in the marine environment is essential [8]. Radionuclides reaching the marine environment may move through seawater-sediment-biota interface. It is therefore, necessary to quantify the distribution of radionuclides in the marine environment to assess radiological impacts of the detected radionuclides on human health [9]. Keeping this in view radiological studies were carried out in seawater and sediments at Gwadar coast. It is for the first time a systematic work on radioactivity analysis for the coastal seawater and sediments of Gwadar coast has been carried out. Such studies for other coastal areas of Pakistan are in progress. Recently, International Atomic Energy Agency (IAEA), under its Regional Cooperation Agreement (RCA), jointly with United Nations Development Programme (UNDP), has initiated a project on management of marine coastal environment and its pollution. As a component of this project, existing data on marine radioactivity for Asia Pacific is being compiled as Asia-Pacific Marine Radioactivity Database (ASPAMARD). The data presented here will serve as a baseline for radionuclide concentration in sea sediments and sea water of the study area, and will be included in ASPAMARD [10].

2. Methodology

2.1. Sample collection

Shallow marine coastal sediment and water samples were collected from different locations of Gwadar coast between longitude 62.3^{o}E-62.4^{o}E and latitude 25.1^{o}N-25.2^{o}N, (Fig. 1). Sediment samples were collected from the inter-tidal zone with soil corer. Samples of 1-2 kg were taken. All samples were collected from low tide (ebb-tide) line. Water samples were collected (40-60 litre) and acidified to pH <1 immediately. Samples were contained in high quality plastic cans, sealed, labeled and transported to laboratory for analysis.

The location of each sampling point was monitored with Personal Navigator, GPS-100

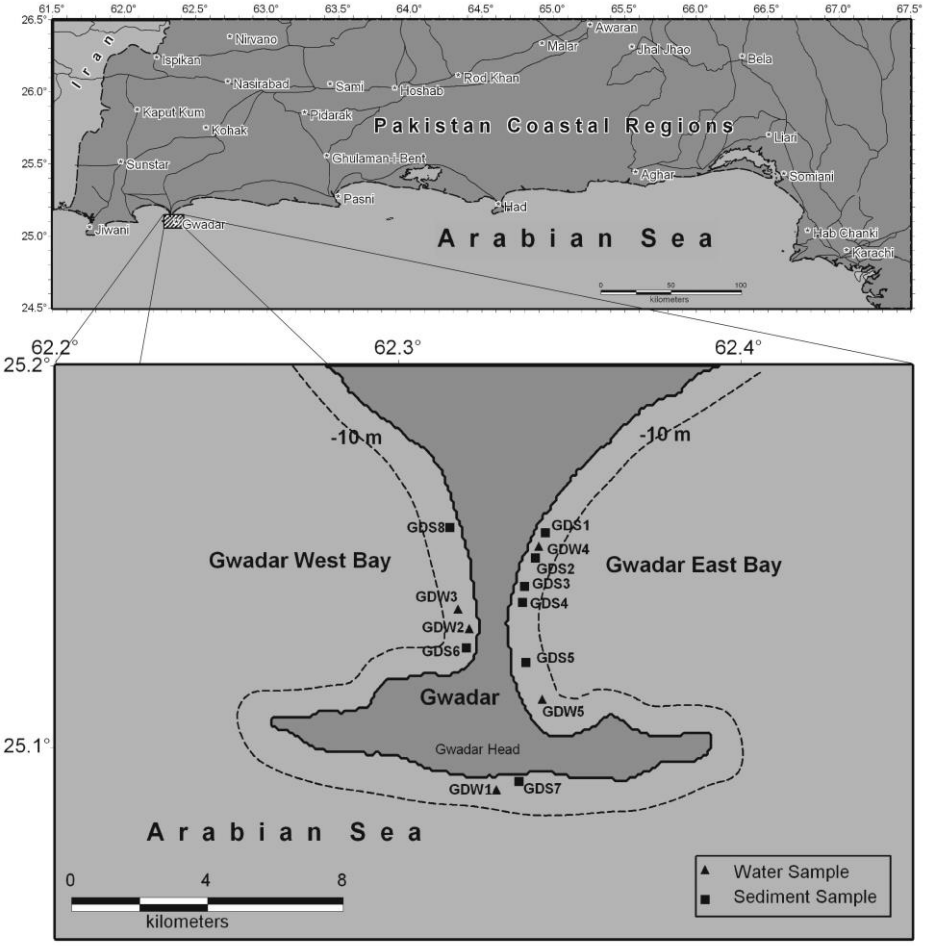

Figure 1. Map showing sampling locations for Gwadar area.

(M/S Garmin, 11206 Thompson Avenue, Lenexa, KS 66219). Geographical locations of the samples collected and reference sites are given in Table 1,

2.2. Sample preparation

Sample preparation like drying, grinding, homogenization and packing in proper geometrical dimensions for gamma spectrometric analysis was carried out for sediment samples. Sediment samples were dried to a constant weight in an oven at 80 ^{o}C, avoiding the loss of any volatile radionuclides. The dried sediments were pulverized and sieved to pass through a 1-2mm mesh. The meshed sediments were transferred to plastic containers of 200-ml capacity for gamma activity analysis. Each sample was carefully sealed for a period of 40 days to attain secular equilibrium between ^{226}Ra, ^{228}Th and their respective progeny required for gamma spectrometry. In case of water, the filtration was carried out using fine membrane filters of 0.45µm pore size. Containers were prewashed with water, detergent and acid. Few milli litters of HNO_3 were added to each water sample to avoid metal precipitation. In the laboratory all water samples were stored under cooled conditions (4-12 °C). Preconcentration of caesium in seawater was performed by chemical separation prior to gamma spectrometric analysis. Caesium was concentrated as its ferrocyanide precipitates. Enough concentrated hydrochloric acid was added into 30 litre water sample in order to make its pH = 2.60 mg of Ni^{+2} was added in it followed by the addition of 3.5 g of potassium ferrocyanide. Stirred and left to settle the precipitates of nickle ferrocyanide overnight. Siphoned off the supernatant and filtered/centrifuged the precipitate containing coprecipitated caesium. Transferred the precipitates onto a crucible and dried at 105 ^{o}C to

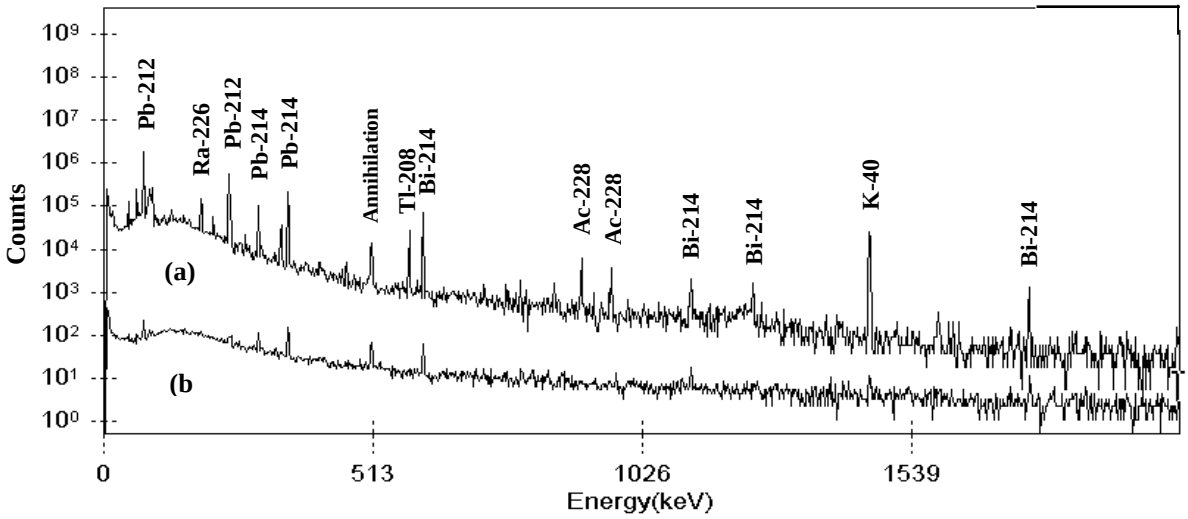

Figure 2. Comparison of gamma spectra: (a) Sediment sample (b) Background of the system.

dryness, ground and determined ^{137}Cs in it by gamma spectrometry.

2.3. Gamma spectroscopic analysis

Gamma spectrometric analysis of the samples was performed with a computer based gamma spectrometry system for qualitative and quantitative determination of gamma emitting radionuclides. System included a high resolution HPGe coaxial detector, high voltage power supply (Model 3106D), fast spectroscopy amplifier (Model 2024), ADC (Model 8713), digital stabilizer (Model 8223) and an AccuSpec-B board Multi Channel Analyzer (MCA) (Model 840633). The whole system including detector and all other modules were from M/S CANBERRA, USA. Detector resolution was 700 eV at 122 keV energy of ^{57}Co. Detector was shielded in a layered circular shield having cavity of 33 cms. dia and 45.7 cms. height. Top loading shielding consists of stacked rings of 10 cms. lead, 5 cms. steel and a copper lining of 5mm thickness. System calibrations and gamma spectrum analysis was carried out by Genie-2000 (CANBERRA) software. A spectrum acquired for a sediment sample of Gawader coast (a), superimposed on the system background spectrum (b) is shown in Fig. 2. The size of the spectral peaks show clearly the presence of natural radionuclides in the sediment sample. The detector was calibrated against IAEA's sea water/sediment reference standards (IAEA-368, IAEA-381) and pure potassium chloride salt, IAEA-RGK-1. The ^{226}Ra and ^{228}Ra activities were estimated by the measurement of their decay products in radioactive equilibrium. For the determination of ^{226}Ra the gamma lines of ^{214}Pb (351.9 keV) and ^{214}Bi (609.3 keV, 1120.3 keV) were used. The gamma ray energies of ^{212}Pb (238.6 keV), ^{228}Ac (911keV) were used to measure the concentrations of ^{228}Ra, whereas ^{40}K activity was determined from the 1460.7 keV emission [11]. For the measurement of ^{137}Cs, its gamma line at 661.6 keV was used. The lower limits of detection of the system for ^{226}Ra, ^{228}Ra, ^{137}Cs and ^{40}K are 8.2 Bq.kg^{-1}, 3.9 Bq.kg^{-1}, 1.3 Bq.kg^{-1} and 19.8 Bq.kg^{-1} respectively. For water, the lower limits of detection of the system for ^{226}Ra, ^{228}Ra, ^{137}Cs and ^{40}K are 0.4 Bql^{-1}, 0.5 Bq.l^{-1}, 0.03 Bq.l^{-1} and 1.8 Bq.l^{-1} respectively.

3. Results and Discussion

Results of sample analysis are reported in Table 2. Activity is reported in Bq.kg^{-1} for sediments (dry weight basis) and in Bq.l^{-1} in case of water.

3.1. Inter tidal sediments

The activity in sediment samples is in the range from 16.9±2.1 to 31.7±3.2 Bq.kg^{-1} for ^{226}Ra, 9.8±1.2 to 13.3±1.2 Bq.kg^{-1} for ^{228}Ra and 152.4±11.4 to 244.4±15.7 Bq.kg^{-1} for ^{40}K. Medians

Table 2. Activity concentration of different radionuclides in sediment and water samples Activity is given in $Bq.kg^{-1}$ for sediments and $Bq.l^{-1}$ for water.

Sample Code	Activity Concentration			
	^{226}Ra	^{228}Ra	^{137}Cs	^{40}K
Sediments				
GDS1	26.4 ± 2.9	10.5 ± 1.3	BDL (< 1.3)	152.4 ± 11.4
GDS2	16.9 ± 2.1	09.9 ± 1.0	BDL (< 1.3)	202.0 ± 13.4
GDS3	23.2 ± 3.2	12.4 ± 1.3	BDL (< 1.3)	221.9 ± 14.7
GDS4	25.2 ± 3.4	11.6 ± 1.8	BDL (< 1.3)	205.8 ± 18.1
GDS5	31.4 ± 2.9	13.2 ± 1.4	BDL (< 1.3)	232.1 ± 13.4
GDS6	19.0 ± 2.8	09.8 ± 1.2	BDL (< 1.3)	243.6 ± 16.3
GDS7	31.7 ± 3.2	13.3 ± 1.2	BDL (< 1.3)	238.28 ± 2.3
GDS8	23.2 ± 3.1	11.7 ± 1.2	BDL (< 1.3)	244.4 ± 15.7
Median value	24.3	11.7	-	227.0
Minimum value	16.9	09.8	-	152.4
Maximum value	31.7	13.3	-	244.4
Seawater				
GDW1	BDL (< 0.4)	BDL (< 0.1)	BDL (< 0.03)	09.3 ± 0.8
GDW2	BDL (< 0.4)	BDL (< 0.1)	BDL (< 0.03)	13.8 ± 2.0
GDW3	BDL (< 0.4)	BDL (< 0.1)	BDL (< 0.03)	13.1 ± 2.9
GDW4	BDL (< 0.4)	BDL (< 0.1)	BDL (< 0.03)	16.6 ± 2.9
GDW5	BDL (< 0.4)	BDL (< 0.1)	BDL (< 0.03)	17.5 ± 3.0

BDL - Below Detection Limit

of activity levels at different locations at Gwadar for ^{226}Ra, ^{228}Ra and ^{40}K are 24.3 $Bq.kg^{-1}$, 11.7 $Bq.kg^{-1}$ and 227.0 $Bq.kg^{-1}$ respectively. These values are in general comparable with results quoted in the literature for other regions of the world. The results of the sediment samples from the Cox's Bazar, Sea beach bay of Bangal are; ^{226}Ra (13.9 to 25.2 $Bq.kg^{-1}$), and ^{40}K (382.9 to 651.9 $Bq.kg^{-1}$) [12]. The value of ^{226}Ra for Pacific Ocean sediments is 21.4 $Bq.kg^{-1}$ [13]. The activity levels for Irish Sea Sediments are; ^{226}Ra (23.9 $Bq.kg^{-1}$), ^{228}Ra (36.7 $Bq.kg^{-1}$), and ^{40}K (560.0 $Bq.kg^{-1}$) [14]. The activity values for ^{226}Ra, ^{228}Ra and ^{40}K for Indian Ocean Sediments are 13.8, 26.7, and 297.0 $Bq.kg^{-1}$ respectively [15]. The range of ^{40}K is 118.3 to 608.2 $Bq.kg^{-1}$ for the Coast of Chittagong, Bay of Bangal [16]. The levels of natural radionuclides in sediments from Turkish coast, Black Sea are; ^{232}Th (17-37 $Bq.kg^{-1}$) and ^{40}K (301-833 $Bq.kg^{-1}$) [17].

3.2. Seawater

For sea water samples, the activity concentration detected for ^{40}K is 9.3±0.8 to 17.5±3.0 $Bq.l^{-1}$. Median activity for ^{40}K for water at Gwadar is 13.8 $Bq.l^{-1}$. Reported value of ^{40}K for Irish seawater is 11.4 $Bq.l^{-1}$ [18].

No artificial radionuclide was detected in any sea sediment or water sample. A graphical presentation for the median of activity levels for sediments of Gwadar coast and some other oceans for the detected radionuclides is given in Figure 3.

In order to assess the health effects from the radioactivity of the surface materials containing ^{226}Ra, ^{232}Th (in equilibrium with its daughter product ^{228}Ra) and ^{40}K, Radium equivalent (Ra_{eq}) activity, air absorbed dose rates (D) and annual effective doses (H) were calculated using the following expressions [19,20,21].

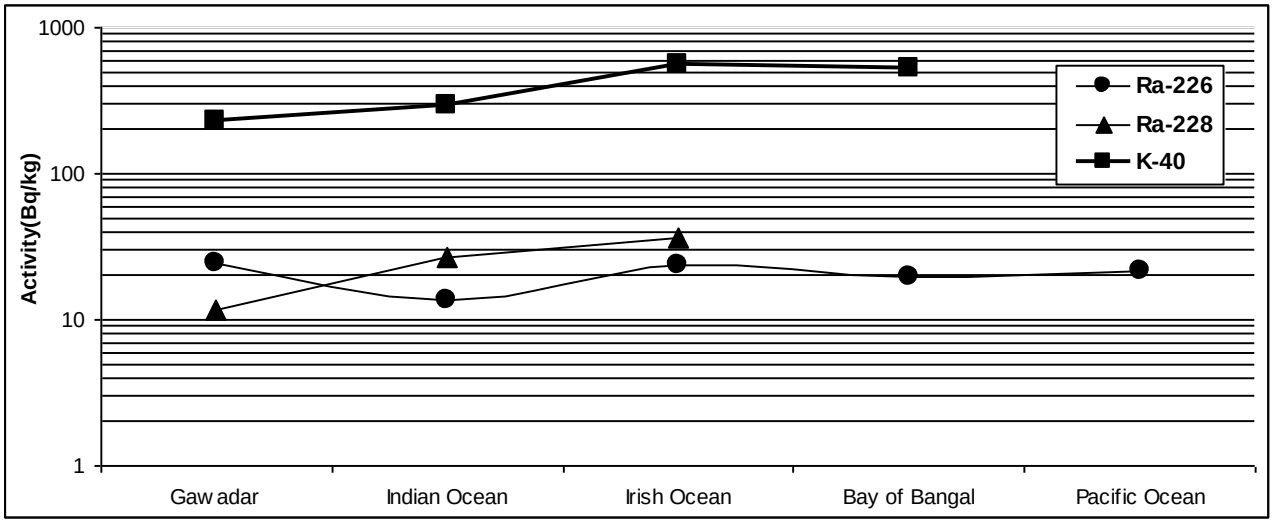

Figure 3. Comparison of median activity of radionuclides in sediments from Gwadar coast with other regions.

$$Ra_{eq} = A_{Ra} + (A_{Th} \times 1.43) + (A_K \times 0.077) \quad (1)$$

$$D = 0.427\ A_{Ra} + 0.662\ A_{Th} + 0.0432\ A_K \quad (2)$$

$$H = D\ (nGy/h) \times 8760\ (h) \times 0.2 \times 0.7\ (Sv/Gy) \quad (3)$$

The annual effective dose for Ra_{eq} of 370 $Bq.kg^{-1}$ corresponds to the dose limit of 1.0 mSv for the general population [22]. The ground materials, for which radium equivalent activity concentration exceeds 370 $Bq.kg^{-1}$ may pose radiation hazards. Ra_{eq} activity for sediments of Gwadar coast is in the range 46.9 ± 2.8 to 69.0 ± 3.9 $Bq.kg^{-1}$ with the mean value of 57.9 $Bq.kg^{-1}$. The measured mean value of Ra_{eq} is found to be less than the value of 370 $Bq.kg^{-1}$.

The absorbed dose rates determined in air at 1 meter above the surface due to gamma radiation determined in sediments, varies from 22.2 ± 1.3 to 32.1 ± 1.7 $nGy.h^{-1}$ with a mean value of 27.1 $nGy.h^{-1}$. The mean values of the air absorbed dose rate at one meter height are in normal range [23].

The range of annual effective doses due to activity concentration of natural radionuclides in sediments is 0.03 mSv to 0.04 mSv with mean value of 0.03 mSv. The mean value is less than the average external gamma dose of 1.0 $mSv.y^{-1}$ from natural radiation sources [24]. As the values of absorbed dose and annual effective dose are calculated for air medium, these values will be even lower due to the radiation attenuation from overlying waters.

4. Conclusion

1. Mean activity concentration of ^{228}Ra and ^{226}Ra in sediment samples of Gwadar coast are comparable with the results of other coasts of the world, whereas, ^{40}K results are found in general to be on the lower side.
2. On the basis of values obtained for Ra_{eq}, air absorbed dose rate and annual effective dose equivalent it is concluded that no harmful radiation effects are posed due to the activity of coastal sediments to the public going for recreation on the beaches or the sailors/fisherman involved in their activities in the area due to the radiation from sediments. The effects due to waterborne activity are negligible as only ^{40}K was detected in low concentrations.

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