Marine Pollution Bulletin 127 (2018) 377–386

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Baseline

Environmental radiation and potential ecological risk levels in the intertidal zone of southern region of Tamil Nadu coast (HBRAs), India

Punniyakotti. J.[a,b], Ponnusamy. V.[a,*]

[a] Department of Physics, Anna University (MIT campus), Chrompet, Chennai 600 044, India
[b] Department of Physics, Meenakshi Sundararajan Engineering College, Chennai 600 024, India

ARTICLE INFO

Keywords:
Radiation
Heavy metal
Ecological risk
Intertidal zone
Tamil Nadu coast

ABSTRACT

Natural radioactivity content and heavy metal concentration in the intertidal zone sand samples from the southern region of Tamil Nadu coast, India, have been analyzed using gamma ray spectrometer and ICP-OES, respectively. From gamma spectral analysis, the average radioactivity contents of ^{238}U, ^{232}Th, and ^{40}K in the intertidal zone sand samples are 12.13 ± 4.21, 59.03 ± 4.26, and 197.03 ± 26.24 Bq/kg, respectively. The average radioactivity content of ^{232}Th alone is higher than the world average value. From the heavy metal analysis, the average Cd, Cr, Cu, Ni, Pb, and Zn concentrations are 3.1, 80.24, 82.84, 23.66, 91.67, and 137.07 ppm, respectively. The average Cr and Ni concentrations are lower, whereas other four metal (Cd, Cu, Pb, and Zn) concentrations are higher than world surface rock average values. From pollution assessment parameter values, the pollution level is "uncontaminated to moderately contaminated" in the study area.

The marine ecosystem is the largest ecosystem after the whole of planet Earth because water accounts for > 70% of the Earth's surface. It is a well-known fact that if the quantity of naturally occurring primordial radionuclides (^{238}U, ^{232}Th, and ^{40}K) and heavy metals present in the intertidal zone sands exceed more than prescribed safe limits, they might pose environmental radiation and metal pollution effects to marine organisms and the marine ecosystem. A scientific study on the distribution of primordial radionuclides in intertidal sediments that would help in assessing the bioaccumulation of daughter products of the primordial radionuclides in the marine organisms assumes importance because of their toxic nature. This is especially due to the transportation and concentration of these radionuclides by physical, chemical, and biological processes. Human exposure to ionizing radiation is one of the scientific subjects that has attracted public attention because radiations of natural origin are responsible for most of the total radiation exposure to the human population. Knowledge of the natural radiation level and distribution of primordial radionuclides in all types of coastal environments that include intertidal zones is important for assessing the effect of radiation exposure on members of public and marine ecosystem. In a coastal environment, radioactive isotopes can be attached to particulate matter in water. Some isotopes remain dissolved and are termed conservative within water. Others are scavenged out of solution onto particulate materials by biological or chemical process, e.g., adsorption and co-precipitation. They may be deposited in sediments on the bottom of the sea. Uranium and thorium radionuclides have different behavior in the marine environment. Uranium remains dissolved in water, while thorium is a particularly insoluble element in natural waters, and it is usually found in association with solid matter (El-Taher and Madkour, 2011). The solubility characteristics of radionuclides and getting deposited in the beach sands of intertidal zone play a predominant role in aquatic radioecology. Hence, it assumes importance to monitor the intertidal zone also, from the point of view of transport of radionuclides and their deposition in the adjoining beach sands. In recent years, studies on the high natural background radiation areas (HBRAs) in the world have been of prime importance for the risk estimation because of long-term low-level whole body exposure to the members of public. A higher level of natural radiation is observed and reported in many areas in the world such as Australia, Brazil, China, India, Iran, and Japan (Roser and Cullen, 1964; Wei et al., 1993; Ghiassi-nejad et al., 2002; Mishra, 1993 and Sunta, 1993). In India, the monazite placers along the Kerala coast and southernmost tip of Tamil Nadu coast are prominent HBRAs. Although quantification of radioactivity content of the primordial radionuclides and the associated dose rates have been carried out in the southwest coast of Kerala (Shetty et al., 2011 and Ramasamy et al., 2014), the same was not done for the southernmost region of Tamil Nadu coast. Tamil Nadu has a coastal length of about 1000 km encompassed in thirteen coastal districts. Out of the thirteen coastal districts, the natural radioactivity content and the associated dose rates had already been established for seven coastal districts covering the

* Corresponding author.
E-mail addresses: vps@annauniv.edu, ponnu76@rediffmail.com (V. Ponnusamy.).

https://doi.org/10.1016/j.marpolbul.2017.11.026
Received 10 June 2017; Received in revised form 8 November 2017; Accepted 13 November 2017

northern region of Tamil Nadu coast (Ramasamy et al., 2012; Satheeshkumar et al., 2012 and Ravisankar et al., 2015). In the present study, the remaining six coastal districts of the southern region of Tamil Nadu are considered, covering about 500 km of coastal length from Thanjavur to Kanyakumari. Because a similar study on environmental radioactivity monitoring of the intertidal sand samples with high background area from the southern region of Tamil Nadu coast is not available, the same has been undertaken.

Heavy metal pollution and its associated risks in a marine environment are due to the rapid increase in industrialization, fast development of economics, urbanization, population growth, and agricultural activities. Cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn) are some of the most common heavy metal pollutants of concern (Wenfeng et al., 2012). Metals have low solubility in water and can be adsorbed and accumulated on the bottom sediments, which act as sinks (Suresh et al., 2011). Heavy metals pose a potential threat to ecological system and human health because of their toxicity, persistence, and bioaccumulation and biomagnification through food chains (Suresh et al., 2015). Sediment analyses play a crucial role in assessing the degree of heavy metal pollution and resulting health risks associated with the food chain. Heavy metal concentrations have been studied in the coastal sands of many countries including India (Fukushima et al., 1992; Zhou et al., 2007; Azhar et al., 2009; Guo et al., 2010; Bashir et al., 2011; Wenfeng et al., 2012; Subramanian and Mohanachandran, 1990; Manjunatha et al., 1996; Jonathan and Ram Mohan, 2003; Srinivasa et al., 2004; Selvaraj et al., 2003; Ayyamperumal et al., 2006; Satpathi et al., 2012; Venkatachalapathy et al., 2011; Suresh et al., 2015 and Madhuparna et al., 2015).

India has a long coastal line of 7516 km, and of this, the southwestern and eastern coastal regions are rich in estuaries, mangrove areas, marine algae, marine fauna, lagoons, major ports, and fishing activities (Jonathan et al., 2008). Especially in the present study area of the southern region of Tamil Nadu coast, the trace of mangroves were affected by chemical wastes from the aquaculture farms in Thanjavur and Pudukottai coastal districts. Ramanathapuram district has rich coastal bio-diversity, and unique coral reefs are found in the Gulf of Mannar region on one part of its coast. In Tuticorin, Tirunelveli, and Kanyakumari coastal districts, the location of harbor, thermal and nuclear power plants, and associated fishing activities combined with heavy vehicular traffic are the major contributors (Punniyakotti and Ponnusamy, 2017). In this study area, the river estuary adds additional stress to the marine ecosystem. Therefore, the accumulation of heavy metals should necessarily be monitored in the southern region of Tamil Nadu coast, India. A comprehensive baseline study on assessing the prevailing radiological and toxicological parameters in the intertidal sand samples of Tamil Nadu coast is important for mitigating the marine ecosystem and the long-term improvement of public health, if needed. The catastrophic tsunami waves that swept the Tamil Nadu coast during December 2004 could have completely or at least partially altered the natural radioactivity profile, and hence, the present study would also be of great value addition.

Tamil Nadu has a coastal length of about 1000 km encompassed in thirteen coastal districts as shown in Fig. 1. The present study area covers a total coastal length of about 500 km covering six coastal districts, namely Thanjavur, Pudukottai, Ramanathapuram, Tuticorin, Tirunelveli, and Kanyakumari. Fifty sites were selected and numbered as S1 to S50 (Fig. 1). Each sampling site is represented by a village/town and recorded in terms of degree-minute-second [Longitudinal(E) and Latitudinal(N) positions] using a hand-held global positioning system (GPS) unit (Model: GARMIN GPS map76).

For gamma spectral analysis, the collected intertidal zone sand samples were uniformly mixed, sieved, and air-dried and further dried in an oven at 100 − 120 °C for an hour to remove moisture. The samples were stored in an airtight 250-ml plastic container for 1 month, prior to subjecting them to gamma ray spectral analysis. This was to ensure attaining secular equilibrium between radium and its short-lived daughter products. The net weights of the samples were determined before counting (Punniyakotti and Ponnusamy, 2017). A 3″ × 3″ NaI (Tl) scintillation detector was used for gamma spectral measurements. The detector is covered by 150-mm lead shield on all the four sides and at the top. Because of this, the cosmic background is reduced by 98%. The sealed sand samples were placed on the top of the detector, and count spectra were obtained for each beach sand sample. Each sand sample was counted for 10,000 s, and the net radioactivity contents of ^{40}K, ^{232}Th, and ^{238}U were deduced from the count spectra and using the efficiency factor for various energies. The peaks corresponding to 1.46 MeV (^{40} K), 1.764 MeV (^{214}Bi), and 2.614 MeV (^{208}Tl) are considered for the estimation of activity contents. The minimum detectable activity (MDA) of each radionuclide with 95% confidence level (2σ) was determined from the background radiation spectrum obtained for the same counting time as was used for the sand samples. Standard reference sources, procured from the IAEA, RGU1 (uranium ore), RGTh1 (thorium ore), and RGK1 (potassium sulfate) having the certified activities of 1608, 1065, and 4810 Bq, respectively, were used for system calibration and efficiency determination. The estimated MDA values are 2.22 Bq/kg for ^{238}U, 2.15 Bq/kg for ^{232}Th, and 8.83 Bq/kg for ^{40}K.

For heavy metal analysis, sand samples of 0.5 g were digested in microwave teflon vessels. To this, 6 ml of HNO_3 and 2 ml of H_2O_2 and HF each were added to the sand samples, and HF was removed by the addition of an excess of H_3BO_3 (Suresh et al., 2015). After the completion of digestion, the digested samples were made up to 100 ml by diluting it with milliQ water in a polyethylene volumetric flask. One milliliter of the solution was then diluted to 10 ml by adding HNO_3, and the blank solution was also prepared for calibration. All the glassware and plastic containers were washed with 10% HNO_3 solution and rinsed thoroughly with milliQ water. The digested sand sample solution was subjected to the inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer 5300 DV). In this study, six heavy metal (Cd, Cr, Cu, Ni, Pb, and Zn) concentrations were measured. The wavelengths (nm) considered for Cd, Cr, Cu, Ni, Pb, and Zn metals were 228.802, 267.716, 327.393, 231.604, 220.353, and 206.200 nm, respectively. The detection limits (ppm) of the measured heavy metals Cd, Cu, Cr, Ni, Pb, and Zn were 0.0027, 0.0071, 0.0097, 0.015, 0.042, and 0.0018 ppm, respectively. The precision of the analytical procedure was checked by analyzing the standard reference materials of commercially available standards (Merck KGCA, 64,271 Darmstadt, Germany, ICP - Multi element standard solution IV, 23 elements in nitric acid) in triplicates (Suresh et al., 2015).

The distribution of three primordial radionuclides (^{238}U, ^{232}Th, and ^{40}K) in the intertidal zone sand samples of the present study area comprising of 50 sites are shown in Fig. 2. In this figure, the world and Indian average values (UNSCEAR, 2000) are also indicated by horizontal dark and dotted lines, respectively, for comparison. It may be seen from Fig. 2 that, as one moves toward the southernmost region (S26 to S50), the radioactivity contents of ^{238}U and ^{232}Th increase, whereas that of ^{40} decreases. About 90% of the sampling sites (45 out of the 50 sites) have lower radioactivity contents of ^{238}U and ^{40}K, while ^{232}Th activity content is lower in about 70% of sampling sites than both world and Indian average values. The distribution of radioactivity profile indicates that ^{232}Th activity is higher in the southernmost region of Tamil Nadu coast (S26 to S50) and is lower in other coastal sites even though they are also on the same coastal belt. This wide variation in ^{232}Th activity may be attributed to the discontinuous occurrence of monazite and other heavy minerals (Iyengar and Kannan, 1994; Iyer et al., 1974). The extreme radioactivity content values of ^{238}U (370.77 ± 24.54 Bq/kg) and ^{232}Th (3773.60 ± 29.76 Bq/kg) observed at S48 (Lakshmipuram) were excluded while calculating the average value, as indicated in Table 1. It may be observed from Table 1 that the radioactivity contents of ^{238}U, ^{232}Th, and ^{40}K ranged from below detectable level (BDL) to 370.77 ± 24.54 Bq/kg with an