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The distribution of uranium and thorium in samples taken from different polluted marine environment

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Abstract

Concentrations of uranium and thorium in seawater, sediment and some marine species taken from along the coastal areas of Malaysia were determined spectrophotometrically. The uranium and thorium concentrations in seawater were found to vary ranging from 1.80 to 4.1 and 0.14 to 0.88 μg/L, respectively. The concentration of uranium in sediment samples was reported to range from 3.00 to 6.60 μg/g while those of thorium were slightly lower ranging from 0.01 to 0.68 μg/g. The uptake of uranium and thorium in marine species was found to be rather low. Similar variations in total alpha activities in samples were also observed with the total alpha activities relatively lower than the beta activities in most samples.

Keywords: Uranium; Thorium; Total alpha activity; Total beta activity; Seawater; Sediment; Marine species

1. Introduction

The release of radioactive pollutants from nuclear installations and nuclear-propelled vessels causes the accumulation of certain radionuclides in marine food chains. The radiological impact of radioactive release facilities into aquatic environments can be studied by following the behaviour of fallout radionuclides in the sea, provided that they exist in the same physical and the chemical state. During the last three decades approximately 34 MCi of this radionuclides have been introduced into the atmosphere by nuclear detonations, the larger fraction of it entering into the sea [1].

The elements uranium and thorium display sharply contrasting geochemical behaviour in oxic seawater. This is particularly evident from comparison of their mean residence times with respect to scavenging. Uranium is stably dissolved in oxic seawater as the U(VI) uranyl carbonate species, $UO_2(CO_3)_3^{4-}$, and has a 400,000 year residence time in the oceans while thorium (Th^{4+}) is rapidly removed from solution onto particles with a mean residence time of <100 years. Although U(VI) behaves chemically quite unlike Th, under reducing conditions U may be reduced to the more reactive U(IV) and the two elements may be geochemically similar [2]. The concentration of uranium in seawater is about 3.3 ng/L. However, thorium is not dissolved and deposited at the bottom of sea. The concentration of thorium in seawater is 10 pg/mL [3].

The shore and bottom sediments accumulate radionuclides by sorption from seawater or by sedimentation of suspended radioactive solids. The radionuclides that remain associated with sediments are influenced greatly by the chemical, biochemical and microbiological changes that take place in the environment. In the dynamic process of exchange of these nuclides with other matrices of the aquatic environment, it is the labile components that are involved. In sediments, such labile constituents can be composed of the exchangeable or removable ions on the surface, or the hydrous precipitates that undergo dissolution by the complexing action of the chemicals in the environment [4].

A large number of publications can be found on the uptake, concentration, retention and release of radioactive materials by aquatic organisms, aiming at evaluation of the possible hazards resulting from the uptake of radioactivity by human beings, through the food chain, from aquatic food products [5–8]. In this study, the uranium and thorium concentrations in seawater, sediment and some marine species were determined and total alpha

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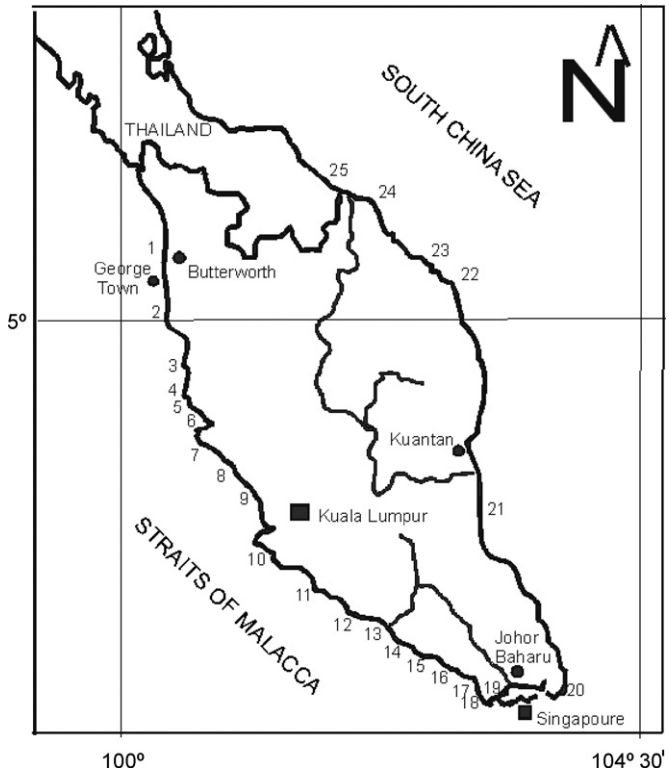

Fig. 1. Map of sampling locations for seawater, sediment and marine samples.

and beta activities in sediment samples and marine species were measured.

2. Experimental methods

2.1. Determination of uranium and thorium

The seawater, sediment and marine samples were collected from 25 sites along the coastal areas of Malaysia. The location of the sampling stations is shown in Fig. 1. Seawater samples were filtered for the removal of suspended matter. The pH of the seawater samples were adjusted with 0.5 M nitric acid to 1.5–2.0. Sediment and marine samples were freeze dried and ground to <200 mesh size. About 1 g of the sediment samples and marine species were placed in a Teflon beaker and evaporated twice to dryness with 10 mL portions of conc. HCl. The residue was then dissolved in 2 mL conc. HCl and 20 mL distilled water and heated while covered for 30 min. The supernatant liquid was decanted into a beaker. The residue was then dissolved in 15 mL of 48% HF acid, 5 mL $HClO_4$ and 10 mL conc. HCl, and evaporated to dryness on a hot plate. Fluoride was removed by three successive evaporations to dryness with 5 mL portions of 6N HCl. The residue was dissolved in 2 mL conc. HCl and 20 mL distilled water and heated for 30 min. The supernatant liquid was combined with the other dissolved portions in a beaker [9]. This procedure was suitable to digest the samples with a yield of $89.69 \pm 3.37\%$.

All of the chemicals used were of analytical reagent (AR) 9 grade. The uranium and thorium concentrations in the samples were determined spectrophotometrically with Arsenazo III ($\varepsilon = 1.09 \times 10^5$ L mol^{-1} cm^{-1}, $\lambda = 658$ nm) [10], ($\varepsilon = 1.27 \times 10^5$ L mol^{-1} cm^{-1}, $\lambda = 665$ nm) [11], respectively. The uranium and thorium concentrations were read off the calibration curve. The results taken are the average of at least duplicate measurements.

2.2. Total alpha and beta activities

The weights of 2 and 1 g of sediment samples and marine species respectively was placed in a planchet. A mixture of UHU glue with acetone (ratio 1:25) was dropped to the planchet and slowly added until the sample is completely submerged. Each sample was dried under an infrared light for 2 h. The alpha and beta activities of these samples were measured using a Canberra 2404 Model counting system. Counting time for each sample was for 30 min. Each count was repeated three times. The detection efficiency of the counting system was determined by counting KCl and U_3O_8 standard samples.

3. Results and discussion

Almost all sea organisms accumulate metals and radionuclides and than also distributed as a result of its physiological mechanism and ecological behaviour. The uptake of metals and radionuclides by sea organisms is normally through water, food and sediment. The relative importance of water and food as sources of metal and radionuclides has changed depending on the exposure conditions and the nature of the elements of interest. Not much is known about the uptake mechanism of metals and radionuclides from sediment. The dynamic process related to the uptake is controlled by means of environmental and fundamental factors such as time of exposure, the physical and chemical nature of pollutants, saltiness of seawater, temperature, competition effects of other elements, microorganisms present, physiology, type of food and life cycle. Organisms that accumulate large amounts of radioactive materials according to the concentration of radionuclides present in seawater; and which are lost slowly are classified as ‘bio-indicators’.

Bio-indicator organisms are used to trace the occurrence of pollution by radioactive or non-radioactive elements and some other chemical wastes. Organisms such as mussel, oyster and comb that concentrate radionuclides from phytoplankton and detritus in seawater can be used as ‘indicator organism’. It is assumed that about 90% of the primary production in sea is formed from phytoplankton organisms. Phytoplankton organisms that are formed will first enter the food chain will accumulate stable and non-stable radionuclides directly. These organisms will concentrate the radionuclide through the adsorption of ionic radionuclides and also by surface adsorption of particular radionuclides. Radioactive and non-radioactive pollutants concentrated in these organisms will enter the human tissue directly or indirectly [12].

3.1. Determination of uranium and thorium

The uranium and thorium concentrations in seawater, sediment samples and marine species collected from the 25 sampling

Table 1
Concentrations of uranium in marine samples

Sample location	Seawater (μg/mL)	Sediment (μg/g)	Marine species			
			KRG (μg/g)	KPG (μg/g)	TRM (μg/g)	KPH (μg/g)
1	2.38 ± 0.01	3.80 ± 0.00	1.92 ± 0.01	2.46 ± 0.00		
2	2.37 ± 0.00	4.33 ± 0.06	1.96 ± 0.00			
3	2.86 ± 0.03	3.72 ± 0.03	2.25 ± 0.00			
4	2.03 ± 0.01	4.30 ± 0.03	2.32 ± 0.01			
5	2.11 ± 0.00	3.02 ± 0.03	2.85 ± 0.01			
6	1.95 ± 0.01	4.21 ± 0.00	1.89 ± 0.01			
7	3.16 ± 0.03	4.53 ± 0.03	2.49 ± 0.03			
8	2.49 ± 0.00	4.24 ± 0.03	2.54 ± 0.03			
9	2.09 ± 0.01	4.59 ± 0.03	2.24 ± 0.01			
10	2.03 ± 0.01	4.75 ± 0.17				2.30 ± 0.01
11	2.19 ± 0.00	4.42 ± 0.15		1.93 ± 0.03		
12	2.38 ± 0.01	3.98 ± 0.06		2.38 ± 0.01		
13	1.86 ± 0.01	3.54 ± 0.03	2.53 ± 0.01	2.22 ± 0.03		
14	2.14 ± 0.00	3.31 ± 0.03	2.18 ± 0.01			
15	1.81 ± 0.00	3.54 ± 0.03		2.03 ± 0.04		
16	2.35 ± 0.01	3.75 ± 0.00		2.81 ± 0.03		
17	3.01 ± 0.00	4.18 ± 0.03	2.79 ± 0.01			
18	2.43 ± 0.03	3.40 ± 0.06		2.82 ± 0.01		
19	2.78 ± 0.00	5.26 ± 0.00		2.12 ± 0.01		
20	2.66 ± 0.00	5.82 ± 0.03		2.31 ± 0.00		
21	2.47 ± 0.01	5.55 ± 0.06	2.81 ± 0.03			
22	2.25 ± 0.03	5.35 ± 0.03			2.05 ± 0.00	
23	3.51 ± 0.00	5.76 ± 0.03	2.03 ± 0.01		2.49 ± 0.03	2.29 ± 0.02
24	4.09 ± 0.03	6.66 ± 0.00			2.46 ± 0.00	2.31 ± 0.00
25	2.72 ± 0.00	6.25 ± 0.06	2.78 ± 0.00		2.03 ± 0.01	2.41 ± 0.01

KRG: blood clam (*Anadara granosa*); KPH: swamp cerith (*Corce scriata*); KPG: mussel (*Perna viridis*); TRM: oyster (*Ostrea folium*).

Table 2
Concentrations of thorium in marine samples

Sample location	Seawater (μg/mL)	Sediment (μg/g)	Marine species			
			KRG (μg/g)	KPG (μg/g)	TRM (μg/g)	KPH (μg/g)
1	0.55 ± 0.01	N.D.	0.01 ± 0.00	N.D.		
2	0.31 ± 0.01	0.12 ± 0.00	N.D.			
3	N.D.	N.D.	N.D.			
4	0.06 ± 0.00	0.14 ± 0.03	N.D.			
5	0.43 ± 0.00	N.D.	N.D.			
6	0.18 ± 0.04	0.30 ± 0.03	N.D.			
7	0.83 ± 0.00	N.D.	N.D.			
8	0.02 ± 0.01	N.D.	N.D.			
9	0.10 ± 0.01	N.D.	N.D.			
10	N.D.	0.68 ± 0.03				0.17 ± 0.11
11	0.44 ± 0.01	0.20 ± 0.03		N.D.		
12	0.46 ± 0.03	0.01 ± 0.00		N.D.		
13	0.28 ± 0.01	0.20 ± 0.03	N.D.	N.D.		
14	0.51 ± 0.00	0.22 ± 0.00	N.D.			
15	0.23 ± 0.04	0.14 ± 0.03		N.D.		
16	0.58 ± 0.01	0.36 ± 0.03		N.D.		
17	0.14 ± 0.00	0.36 ± 0.03	N.D.			
18	0.88 ± 0.00	0.20 ± 0.03		0.12 ± 0.00		
19	0.44 ± 0.01	0.01 ± 0.00		N.D.		
20	0.35 ± 0.00	0.14 ± 0.03		N.D.		
21	0.60 ± 0.01	0.65 ± 0.00	N.D.			
22	0.20 ± 0.01	0.36 ± 0.03			0.06 ± 0.00	
23	0.18 ± 0.01	0.22 ± 0.00	N.D.		0.12 ± 0.05	N.D.
24	0.14 ± 0.00	0.25 ± 0.03			N.D.	0.01 ± 0.00
25	0.68 ± 0.01	0.46 ± 0.03	N.D.		N.D.	N.D.

KRG: blood clam (*A. granosa*); KPH: swamp cerith (*C. scriata*); ND: not determined; KPG: mussel (*P. viridis*); TRM: oyster (*O. folium*).

sites are shown in Tables 1 and 2. The purpose of this determination was to characterize the distribution and accumulation of uranium and thorium in the seawater, sediment and some of the marine species along the coastal areas of Malaysia.

Uranium and thorium concentrations in the seawater from these sampling points are generally low. The U content is a few times larger than the Th content for each of the seawater samples as shown in Table 1 (for uranium) and Table 2 (for thorium). There are a few localities having slightly higher uranium and thorium concentrations for seawater samples, especially locations 23 and 24 for uranium and locations 7 and 18 for thorium. The uranium and thorium concentrations determined varied ranging from 1.80 to 4.1 and 0.14 to 0.88 μg/L, respectively.

These results can be compared also with those of trace elements (Cd, Co, Cu, Hg, Mn, Th, U, V, Zn) in seawater samples which have been analyzed by preconcentration neutron activation analysis according to that of Rao and Chatt [13], and the authors have reported values of 3.1 ± 0.1 and 3.2 ± 0.1 μg/L for uranium concentrations and 1.12 ± 0.11 and 1.29 ± 0.1 μg/L for thorium concentrations in Nearshore and Halifax nearshore seawater samples, respectively. The determination of U and Th concentrations in river water has been studied by Habib and Minski [14]. Average concentrations and range of the uranium and thorium in river water found were 0.4, 0.002–5 μg/L and 0.03, 0.007–0.1 μg/L, respectively.

In all the areas, similar variations in the concentrations of uranium and thorium in sediment samples were observed. The concentration of uranium in sediment samples was found in the range of 3.00–6.6 μg/g. The U concentration in the northeast Malaysian coastal areas was observed to be higher than other locations. The concentration of thorium in sediment samples was slightly lower and ranging from 0.01 to 0.68 μg/g. Results from this experiment showed that the uptake of uranium and thorium in marine species from sediment and seawater were very low compared to the presence of these radionuclides in seawater and sediment. The presence of uranium was more pronounced than thorium in the all four species. The concentrations determined were related to the location of samples. Other factors, such as local environment, lithology and the siting of industries in this area, probably play an important role. The elevated values of uranium and thorium at some sites could be associated with natural processes and sometimes other activities such as mining and the use of fertilizers in the agriculture sector. Seasonal variations in the radioactivity of the top and bottom sediment should be investigated. Also, for the evaluation of radioactive pollution of marine sediments, the radionuclide sorption capability of the sediment should be taken into consideration. Seawater and sediment can be a source of contamination for marine life and aquatic organisms. Water from streams, lakes and ponds should also be considered as another source of contamination for the species.

3.2. Total alpha and beta activities

It can be observed from Tables 3 and 4, that there are a few localities having slightly higher total alpha and beta radioactivity values for sediment samples, especially locations 2, 10, 11, 21, and 25, while there is a wide range of low values in the northwestern and southern part of the Malaysian coast. It was seen that

Table 3
Total alpha activities in marine samples

Sample locations	Sediment (Bq/g)	Marine species			
		KRG (Bq/g)	KPG (Bq/g)	TRM (Bq/g)	KPH (Bq/g)
1	0.07	0.09	0.05		
2	0.37	0.10			
3	0.31	7.78×10^{-3}			
4	0.29	0.08			
5	0.28	0.07			
6	0.36	0.06			
7	0.21	N.D.			
8	0.22	N.D.			
9	0.27	0.02			
10	0.74				0.07
11	0.35		0.03		
12	0.30		0.06		
13	0.25	0.09	0.06		
14	0.18	0.02			
15	0.24		0.01		
16	0.26		0.03		
17	0.22	0.04			
18	0.23		N.D.		
19	0.17		0.07		
20	0.16		0.07		
21	0.36	0.04			
22	0.27			7.78×10^{-3}	
23	0.15	0.15		1.87×10^{-2}	0.04
24	0.24			0.14	0.12
25	0.37	0.05		0.04	0.05

KRG: blood clam (*A. granosa*); KPH: swamp cerith (*C. scriata*); ND: not detected; KPG: mussel (*P. viridis*); TRM: oyster (*O. folium*).

Table 4
Total beta activities in marine samples

Sample locations	Sediment (Bq/g)	Marine species			
		KRG (Bq/g)	KPG (Bq/g)	TRM (Bq/g)	KPH (Bq/g)
1	0.65	0.24	0.25		
2	0.65	0.17			
3	0.63	0.12			
4	0.75	0.20			
5	0.71	0.27			
6	0.76	0.23			
7	0.66	0.23			
8	0.61	0.20			
9	0.62	0.29			
10	1.71				0.18
11	0.70		0.20		
12	0.67		0.18		
13	0.70	0.31	0.20		
14	0.42	0.16			
15	0.68		0.11		
16	0.54		0.14		
17	0.58	0.13			
18	0.51		0.17		
19	0.29		0.26		
20	0.33		0.15		
21	0.77	0.18			
22	0.74			0.20	
23	0.55	0.13		0.10	0.19
24	0.67			0.10	0.24
25	0.78	0.07		0.20	0.28

KRG: blood clam (*A. granosa*); KPH: swamp cerith (*C. scriata*); KPG: mussel (*P. viridis*); TRM: oyster (*O. folium*).

these low values obtained in sediment samples corresponded to values obtained in marine species. The alpha activity values for marine species were also very low and the beta activity values were found in the range 0.10–0.25 Bq/g.

In general, it appears that the highest alpha activities in sediment samples were found at location 10. This site which is located in the east of Malaysia shows an activity of 0.74 Bq/g which was attributed to the nature of the sediment. Also it was found that the concentration of thorium in seawater was higher at this location.

The alpha and beta activities in sediments range between 0.07–0.74 and 0.29–1.71 Bq/g, respectively. The variability in activity values could be explained by textural characteristics and geochemical composition or both. It is suggested that the study of radioactivity should be investigated together with the geological structure and mineral composition of samples at all these locations. Another factor which should be taken into consideration is the different behaviour of radionuclides in the sediment.

The low alpha activity values found in four marine species studied were compared with those found in sediment. In general, the beta activity values were relatively higher than those of alpha in all the samples. The accumulation of radioactive materials in marine species was rather low compared to the total alpha and beta activities in the sediments taken from the same location.

The estimation of radiation doses to man resulting from the radioactivity introduced into the sea is of great importance since the sea is an important source of livelihood to the Malaysian

Table 5
U and Th dependency obtained from ANOVA test

Sediment	*F*-value	*p*-Value	U dependency
Seawater	13.956	0.010	Very significant
Marine species	0.033	0.858	Not significant
Total alpha activity	0.125	0.727	Not significant
Total beta activity	0.042	0.843	Not significant
Sediment	*F*-value	*p*-Value	Th dependency
Seawater	0.754	0.398	Not significant
Marine species	1.154	0.361	Not significant
Total alpha activity	11.551	0.003	Very significant
Total beta activity	0.665	0.002	Not significant

fishermen. Existing radiological data on seawater, sediment and marine species are sparse but a systematic determination should be performed later. However, results from this work indicate that measurable low α-particle activity was seen in the samples. Although the differences are not known to be significant, they can be indicators of areas possibly requiring additional research to determine the pollution status.

3.3. Statistical analysis

A computer software is used to compute ordinary statistics [15]. The relationship between uranium or thorium in sediment materials and the other sample types were tested using the Pearson correlation. Differences in the mean values were evaluated by one-way factorial analysis of variance (ANOVA) for statistical analysis. Probability values of ≤ 0.01 were considered to be significant. The results are given in Table 5. Good rules of thumb for determining significance from calculated F-values are (a) $F < 2$ implies that correlation is not significant, (b) $2 < F < 5$ implies that the correlation is significant, and (c) $F > 5$ implies that the correlation is very significant [16].

From Table 5, it was observed that there is a good U dependency between sediment and seawater and Th dependency shows that the relation between sediment and total alpha activity.

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