MEASUREMENT OF ^{226}RA IN RIVER WATER USING LIQUID SCINTILLATION COUNTING TECHNIQUE

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ABSTRACT

The presence of ^{226}Ra in water is a great concern in human life since it can cause health risk to a certain extent. In the state of Kelantan, being known of its granitic area, there is a lack measurement of ^{226}Ra content in river water, since water is the major source of water supply. According to the INTERIM National Water Quality Standards for Malaysia (INWQS), ^{226}Ra activity concentration in water cannot exceed 0.1 Bq/L. For this reasons, this research was planned to carry out a systematic measurement of water along Sungai Kelantan. Liquid Scintillation Counting was used for measurement of ^{226}Ra in water samples from Sungai Kelantan mainly in district of Kuala Krai. In this paper, the results obtained is about 26 water samples, filtered and unfiltered, collected along Sungai Lebir, Sungai Sok and Bukit Sabah. Thus, the assessment activity concentration of ^{226}Ra in river water was obtained as well as annual effective dose for consumption of drinking water.

ABSTRAK

Kehadiran ^{226}Ra dalam air mendapat perhatian kerana impaknya yang boleh memberikan kesan tehadap kesihatan pada manusia. Di negeri Kelantan, sebuah negeri yang mempunyai struktur tanah dari batuan granit, belum mempunyai data tentang ^{226}Ra khususnya di dalam air sungai, kerana ia merupakan sumber bekalan air. Merujuk pada "INTERIM Standard Kualiti Air Kebangsaan untuk Malaysia (INWQS)", kepekatan aktiviti ^{226}Ra dalam air tidak boleh melebihi 0.1 Bq/L. Oleh sebab itu, kajian ini dijalankan di sepanjang Sungai Kelantan. Kaedah Pengiraan Sintilasi Cecair telah digunakan untuk pengukuran kepatan aktiviti ^{226}Ra dalam air yang diambil daripada Sungai Kelantan terutama dalam daerah Kuala Krai. Dalam penulisan ini, keputusan yang diperolehi daripada 26 sampel air, yang dituras dan tidak dituras, diambil di sepanjang Sungai Lebir, Sungai Sok dan Bukit Sabah.

Dengan demikian, kegiatan penilaian konsentrasi ^{226}Ra dalam air sungai serta dos berkesan ta hunan untuk konsumsi air minuman didapatkan.

Keywords: Liquid Scintillation Counting, ^{226}Ra activity concentration, Kelantan River

INTRODUCTION

The issue of river pollution is not new to a general public in this country, but what is new to them is the presence of natural radionuclide in water body such as radium radioisotopes. ^{226}Ra and ^{228}Ra is the decay products of ^{238}U and ^{232}Th respectively that exist naturally in soil, rocks and water including ground water and underground water. Rivers, being the major sources of water supply in the country, are subjected to this type of contaminants. As being set in the interim water quality parameters, radium radioisotopes should be less than 0.1 Bq/L (National Water Quality Standards for Malaysia, 2009). Department of Environment (DOE) has done classification of the rivers in Malaysia according to the degree of pollution. There are some rivers which are badly polluted, but the presences of radionuclides were never studied. In this study, the main focus is to determine the level of ^{226}Ra in the river water. Kelantan River was chosen for a simple reason because of the geological nature of Kelantan.

Kelantan has two main tributaries which are Lebir River and Galas River converges into single flow, as of the beginning of the Kelantan River. However, those two rivers themselves have many tributaries such as Pergau, Chiku, Nenggiri, Aring and Pertang River (virtualmalaysia.com).

The geological feature of Kelantan is granitic soil with the mixture of shale, limestone and mudstone. Granite rocks are natural sources of the radiation and usually have high radioactivity. Mostly granite rocks are formed from magma due to the temperature, depth, time and the mineral itself. Some granite contains higher concentration of uranium deposit. Uranium and thorium are two radioactive elements found naturally in the earth's crust. Uranium and thorium are generally enriched in the youngest, most felsic and most potassic members of comagmatic suites of igneous rocks such as granites (Rogers and Adams, 1969). The solubility of uranium in soil is dependent on several factors such as pH, redox potential, temperature, soil texture, organic and inorganic compounds, moisture and microbial activity (Rivas, 2005). The uranium present in rocks and soil as a natural constituent represents natural background level. Thus, natural processes of wind and water erosion, dissolution, precipitation, and volcanic action acting on natural uranium in rock and soil redistribute far more uranium in the total environment than the industries in the nuclear fuel cycle (Birke *et. al*., 2010).

Radioactivity is energy given off during the spontaneous decay of unstable atoms called radionuclides. Due to the geological conditions of granitic rocks, Kelantan has a high possibility of the presence of radionuclides that show up in water from the erosion. Uranium is naturally occurring as a mineral deposit in bedrock, which can become dissolved into water supplies that travel through the fractures of bedrock, coming in contact with the mineral. Through times, those uranium decays to more stable element, radium. The EPA standard for total amount of radium in drinking water is 5 pCi/L i.e. ^{226}Ra and ^{228}Ra. According to the Interim National Water Quality Standards for Malaysia (INWQS), ^{226}Ra activity concentration in water cannot exceed 0.1 Bq/L. It has been a great concern as ^{226}Ra is a radiotoxic, an α-emitter, that it has a long half life which is 1600 year and it can accumulates in human bone, giving higher risk to cancer (Villa *et. al*., 2005).

Determination of ^{226}Ra activity concentration in environmental sample can be determined using many methods such as liquid scintillation counting (LSC), α and γ spectrometry. However, LSC is better comparing to both other methods as it is no-self absorption effects, high efficiency, low background and simple rapid method. As for γ spectrometry, the results obtained must be properly corrected due to self-absorption effects and long counting time to obtain adequate limits of detection. On the other, a radiochemical procedure for α-spectrometry is tedious and time consuming (Villa *et. al*., 2005).

This paper presents the activity concentration of ^{226}Ra in river water from small regions of Kuala Krai as well as the estimated annual effective dose in mSv/yr to compare with the INTERIM National Water Quality Standards for Malaysia (INWQS).

METHOD

Sampling Site

A geological map of Kelantan area showing the 10 district areas is presented in Figure 1. The main geological features in Kelantan are the acid intrusive rocks (undifferentiated), Triassic and Permian. The locations of river water sampling in Kuala Krai district is shown in Figure 2.

River Water samples

For the determination of ^{226}Ra in river sample, about 10 L of raw sample was collected in polyethylene bottle that have been washed with HNO_3 and distilled water. The water samples are taken at the mid depth of the river to ensure that the samples are representative and the element of interest such as radionuclides are included. Concentrated HNO_3 is added to the raw sample as soon as possible in ratio of 1 ml HNO_3 in 1 L water to preserve the water and prevent the loss by sorption of the radionuclides in the bottles (Oliveira *et. al*., 2001). Those samples are taken at the mid depth of the river ranging between 0.01 and 0.3 meter. The sampling activity started in late December 2009 until March 2010.

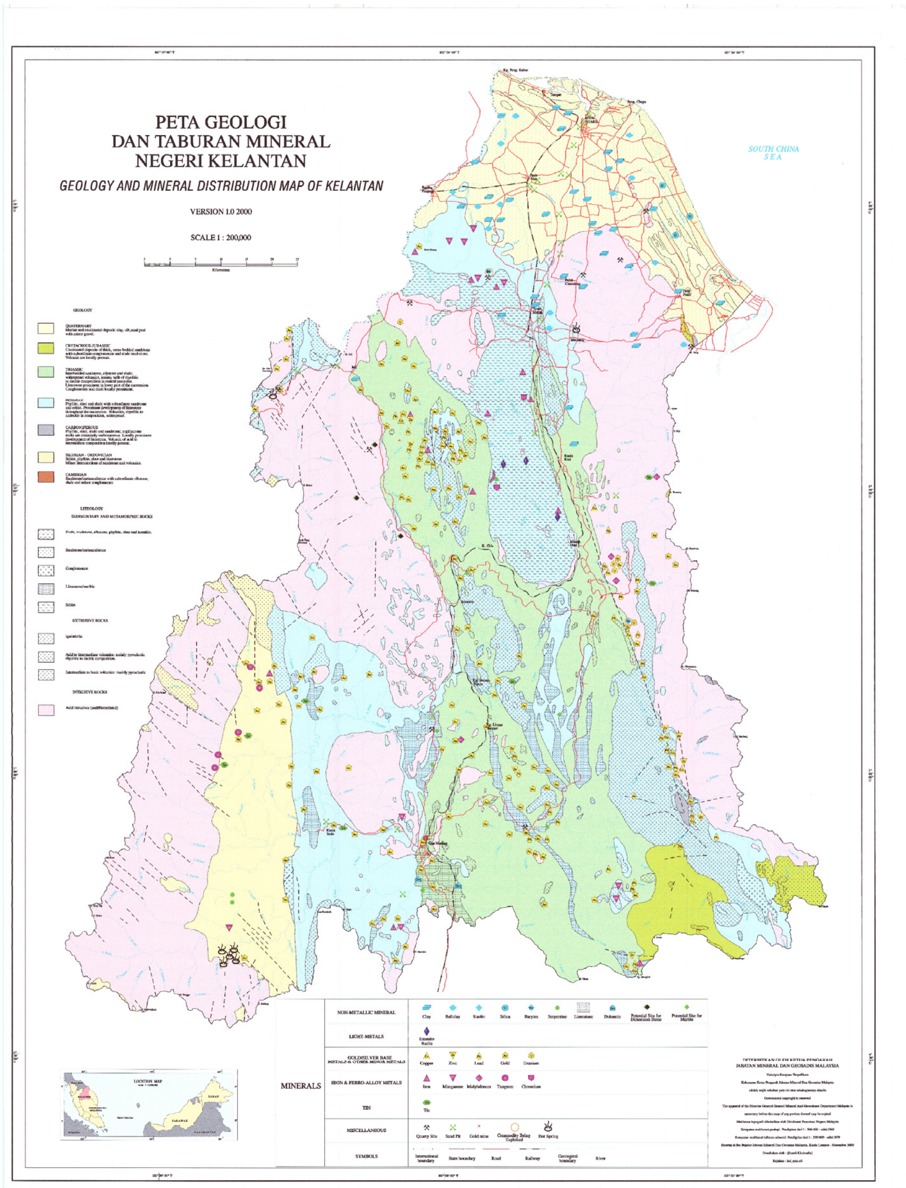


Figure 1: Geological Map of Kelantan

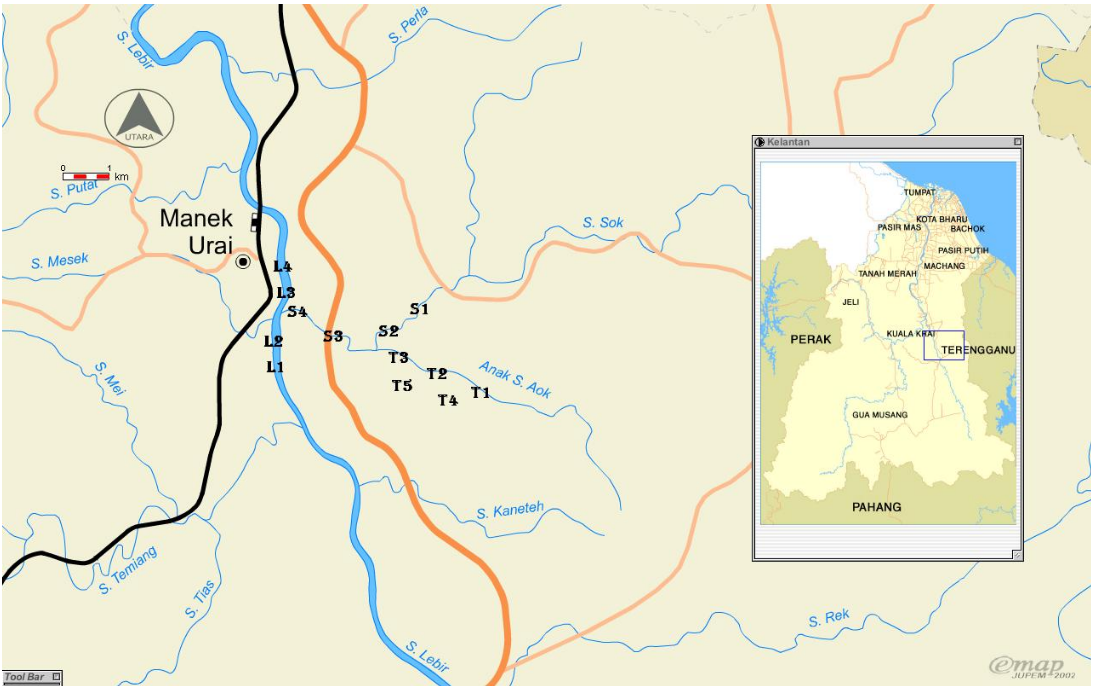


Figure 2: Area of Sampling

Those samples water is filtered through membrane filter with 0.47 µm porosity and 47 mm diameter to eradicate the suspended solid and impurities from water samples. Then, 1L of filtered samples is transferred into Schott bottles and 100 ml of scintillator is added into samples.

Reagents and solutions

Scintillator was prepared by weighing 4.0 g of 2,5-diphenyloxazole (PPO) and 0.4 g of 1,4-bis(5-phenyloxazol-2-yl)-benzene (POPOP) and added into 1 litre scintillation grade of toluene (Borai *et. al*., 2008). This scintillator was stirred for 24 hours to make sure that it's dissolved homogenously in the solvent. Then, 100 ml of scintillator was added to the 1 L water samples and incubated for three weeks. Finally, 20.0 ml liquid scintillation cocktail was transferred into polyethylene vial and measured by LSC immediately.

Table 1: Samples code and coordinates of sampling

Sample	Sample Code	GPS Reading
Lebir River		
Temiang River Filtered	L1	N05°21.253’ E102°14.532’
Lebir River Filtered	L2	N05°22.133’ E102°14.233’
Lebir River 2 Filtered	L3	N05°22.680’ E102°14.332’
Manik Urai Brigde Filtered	L4	N05°23.253’ E102°14.195’
Sok River		
Sok River Filtered	S1	N05°22.514’ E102°16.605’
Sok River 2 Filtered	S2	N05°23.200’ E102°17.063’
Sok River Bridge Filtered	S3	N05°22.789’ E102°16.186’
Sok River Estuary Filtered	S4	N05°22.486’ E102°14’.141’
Small Sok River		
Small Sok River 1 Filtered	T1	N05°22.231’ E102°15.042’
Small Sok River 2 Filtered	T2	N05°22.262’ E102°14.984’
Small Sok River 3 Filtered	T3	N05°22.311’ E102°15.184’
Sabah Hill 2 Filtered	T4	N05°21.372’ E102°17.554’
Sabah Hill 4 Filtered	T5	N05°21.372’ E102°17.426’

Instrumentation

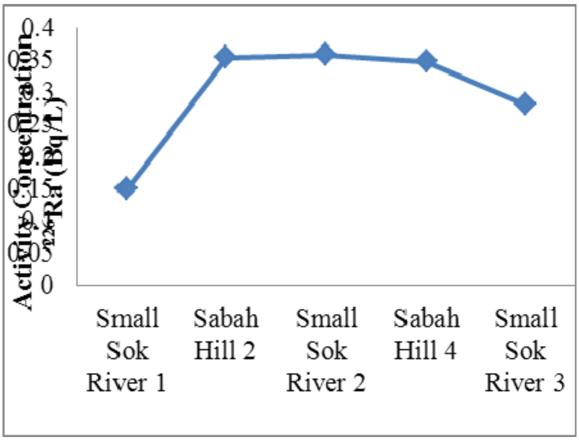
The scintillation cocktail was measured two times for 100 minutes each cycle by using the liquid scintillation counter. The counting was done using protocol 18 of Packard TRICAB 2700 and ^{226}Ra concentration was calculated from the total alpha peaks of ^{226}Ra and its daughters (^{222}Rn) in the alpha spectrum region (Yong, *et. al.*, 2001).

RESULTS AND DISCUSSION

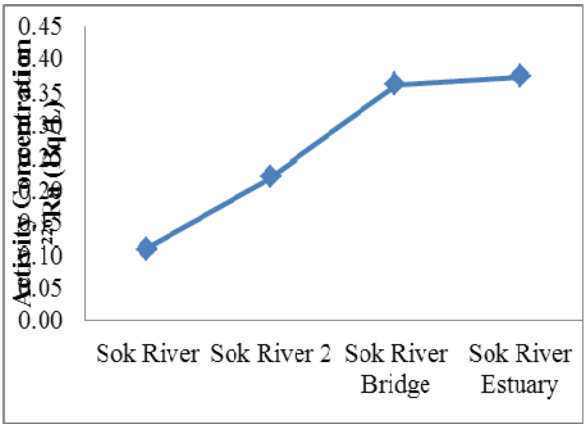
The activity concentrations of ^{226}Ra in 13 locations are presented in Table 1. These activity concentrations are ranging from 0.1095 Bq/L to 0.5483 Bq/L for the filtered. The highest value can be found at Manik Urai Bridge for the filtered sample.

The corresponding result of activity concentrations ^{226}Ra from 13 locations have exceeded the limit set by the INTERIM National Water Quality Standards for Malaysia (INWQS), ^{226}Ra activity concentration in water cannot exceed 0.1 Bq/L. These results indicate that ^{226}Ra is dissolved in water rather than just being attached to the suspended solid.

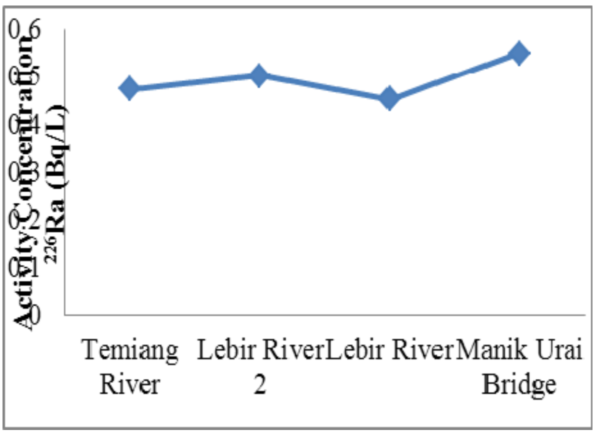
There are three different sections of sampling namely small Sok River joining the Sok River and later joining the Lebir River. The nature of these rivers is from the small stream the water flows into slightly bigger stream and then goes into a big river. From the data obtained, it seems that all sections show a similar trend where the ^{226}Ra activity concentration in each river section is increasing when the water move towards the downstream of the river system. Along the way, there may be accumulation of ^{226}Ra in the water due to erosion along the river basin. Figures 3(a) to 3(c) show the activity concentrations of ^{226}Ra measured in all of the sections in the study area.



(a)



(b)



(c)

Figure 3: Activity concentrations of ^{226}Ra measured along the 3 river sections in the study area

Figure 4 shows the activity concentration of ^{226}Ra along the three sections in the study area. The activity concentration of ^{226}Ra shows a trend where the sample from the downstream has the highest activity. It seems different tributaries contribute different amount of ^{226}Ra depending on the geological nature of the river basin. Further study need to be carried out in order to trace the major source of radium along this river.

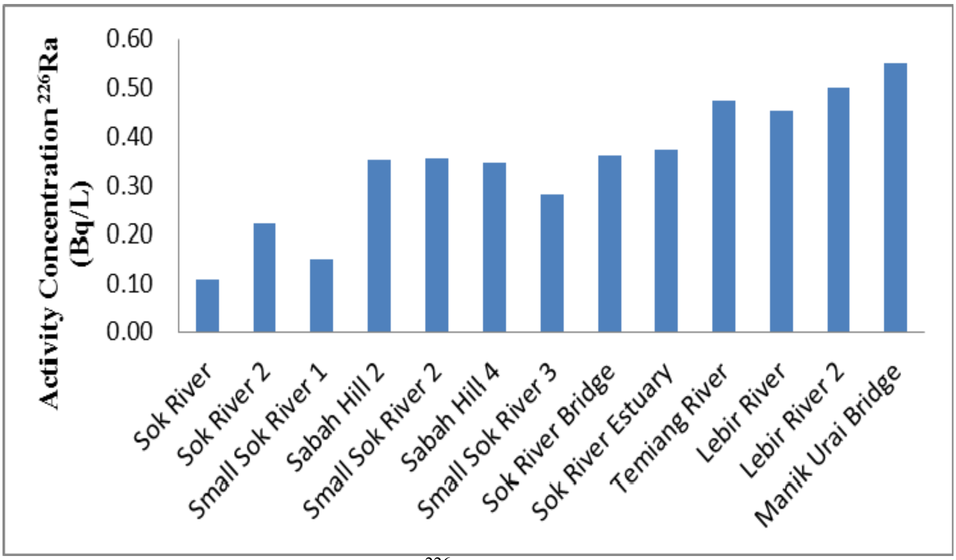


Figure 4: Activity concentration of ^{226}Ra along 3 different sections in the study area

Generally, the samples have ^{226}Ra activity concentration of more than the limit set in INWQS. The reason for this is because the area (river basin) is within the granitic region which contributes some amount of natural radionuclides. Two major radioisotopes that has a very significant role in this are ^{238}U and ^{232}Th. Form their decay products that one can detect ^{226}Ra and ^{228}Ra. Since ^{228}Ra has rather short half life, then it contribution is very much less significant as compared to ^{226}Ra. From the health risk point of view, the daughter of radium i.e. radon and thoron will have more contribution since they are in the form of gas and they also dissolve in water (Table 2).

The assessment of annual effective dose in the river water samples, it is expected that some contribution from the naturally occurring radionuclides in the granitic area and through the decays series of the uranium and thorium in the soils. (Lasheen, *et. al.*, 2007). The annual effective dose is in the range between 0.0224-0.1531 mSv/year (see Table 1) calculated using the equation below.

Annual effective dose: 730 L/yr x 2.8×10^{-4} mSv/Bq x activity concentration of ^{226}Ra (Bq/L)

Table 2: Activity Concentration ^{222}Rn and Annual Effective Dose of ^{226}Ra in river water from different locations in Kelantan

Sample Code	^{226}Ra (Bq/L)	^{222}Rn (Bq/L)	Estimated annual effective dose (mSv/y)
Lebir River			
L1	0.4715 ± 0.050	3.8911 ± 0.41	0.0964
L2	0.4510 ± 0.042	3.7540 ± 0.35	0.0922
L3	0.4998 ± 0.041	4.1577 ± 0.34	0.1022
L4	0.5483 ± 0.033	4.4326 ± 0.27	0.1121
Sok River			
S1	0.1095 ± 0.049	0.8836 ± 0.40	0.0224
S2	0.2203 ± 0.036	1.7834 ± 0.29	0.0450
S3	0.3613 ± 0.039	2.9056 ± 0.32	0.0739
S4	0.3732 ± 0.030	3.0353 ± 0.24	0.0763
Small Sok River			
T1	0.1491 ± 0.045	1.2073 ± 0.37	0.0305
T2	0.3569 ± 0.031	2.8880 ± 0.25	0.0730
T3	0.2803 ± 0.034	2.2652 ± 0.28	0.0573
T4	0.3524 ± 0.033	2.8400 ± 0.27	0.0720
T5	0.3466 ± 0.033	2.8211 ± 0.27	0.0708

Assuming people from this area using the river water as main water supply, annual effective dose for consumption of water for an adult were then calculated. The amount of annual drinking amount is 730 L/yr assuming that adult drinks water for 2L/day and the dose conversation factor for ^{226}Ra is $2.8x10^{-7}$ Sv/Bq (Kozlowska *et. al.*, 2007). According to the Decree of the Polish Ministry of Health (2002), the annual effective dose for all radionuclides except for tritium cannot exceed 0.010 mSv/year (Kozlowska *et. al.*, 2007).

CONCLUSIONS

As conclusions, the concentration of ^{226}Ra in river water samples taken are exceeded the INTERIM National Water Quality Standards for Malaysia (INWQS) which is 0.1 Bq/L. As for annual effective dose for water, the values also have exceeded the international recommended value which is 0.01 mSv/yr.

To the best of our knowledge, this is the first detailed study of radioactivity concentrations ^{226}Ra in the source of drinking water supplies in Kelantan, Malaysia. The data obtained in this study is baseline which can be used to evaluate possible future changes. It should provide a good baseline for setting standards for water quality in this country.

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