

DISTRIBUTION OF Po-210 IN SEAWATER, BIOTA AND SEDIMENT IN THE EAST COAST OF PENINSULAR MALAYSIA

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ABSTRACT

The purposes of this study were to quantify the radioactivity and assess the value of CF and K_d of Po-210 in seawater, biota and sediment samples taken from Pantai Melawi, Tok Bali and Pulau Perhentian areas. These three matrices of marine samples were collected at those areas in 2017 and 2018. In this study, the activity concentrations of Po-210 were measured by using alpha spectroscopy after radiochemical separation and spontaneous deposition processes. The activity concentrations of Po-210 in seawater, biota and sediments were ranged from 0.39 ± 0.02 Bq/L to 2.16 ± 0.09 Bq/L; 4.06 ± 0.11 Bq/kg fw to 67.03 ± 3.00 Bq/kg fw and 35.86 ± 1.60 Bq/kg dw to 69.14 ± 3.09 Bq/kg dw, respectively. Meanwhile, the value of CF and K_d were ranged of 0.22×10^4 L/kg to 10.64×10^4 L/kg and 1.66×10^4 L/kg to 13.23×10^4 L/kg, respectively. The variations of the activity concentration, CF and K_d value of Po-210 probably due to factors of geography region, physical and chemical properties of the ambient water, sediment particle size, affected from terrestrial input, condition of marine environment, species of fishes, food intake pattern, particulate scavenging process, precipitation process and others.

Keywords: Alpha spectroscopy, biota, marine environment, Po-210, seawater, sediment

INTRODUCTION

Polonium-210 (Po-210) is one of the most interesting and important alpha emitters naturally occurring radionuclides and member of ^{238}U decay series due to its relatively high activity concentrations in certain foods and its relatively high ingestion dose coefficient (IAEA, 2017). The knowledge of the concentration and distribution of this radionuclide is interesting since it provides important information for the monitoring of environmental contamination by natural radioactivity (Lubna et al., 2011).

It exists in the environment as a result of the Pb-210 decay within the U-238 decay series with a half-life of 138.4 days and peak energy of 5323 keV. It also presents in the environment from the result of human activities such as mining and combustion of fossil fuels. In regions of uncontrolled mining, contaminations of Po-210 into the water can occur from the discharged of mine water which contains dissolved radionuclides into the nearby water systems. Other than that, increased radiation exposure from the technically enhanced naturally occurring radionuclides material (TENORM) can also be due to the leaching of radionuclides with water from the waste deposited nearby the mining site (Lubna and Mohamed, 2011).

Po-210 enters the marine environment via the natural radioactive decay of Rn-222 gas, Ra-226 in solution and through wet and dry atmospheric deposition of Bi-210 and Pb-210 (Turekian et al.,

1977). Po-210 is supplied to marine water through atmospheric input, rivers and run-off, and the in-situ decay of Ra-226 precursor in the water column (Raja and Shahul Hameed, 2010). Atmospheric deposition is the main source of Po-210 in the ocean waters. However, this indicated a small amount of Po-210 in seawater originates from the atmospheric deposition of polonium itself (Cochran, 1992; Nozaki et al., 1991), but most Po-210 in the marine environment is largely produced by the decay *in situ* of Pb-210 ($T_{1/2}$: 22.3 years) deposited from the atmosphere (Meli et al., 2013). In marine water, Po-210 is non-conservative in its distribution being dependent on its association with suspended particles and biological cycles (Raja and Hameed, 2010). Align with that, only minor latitudinal or temporal gradients and the average activity concentration is estimated to be about 1 ± 0.5 Bq/m³ (Aarkrog et al., 1997). Uptake of cationic Po-210 onto particles (fractionated towards organic phases) and into phyto- and zooplankton results in removal of P-210 from the more productive, shallower marine regions with consequently diminished sea water activities. Scavenging of Po-210 by particles (biased towards inorganic phases) has a smaller, but measurable, effect on Po-210 activities in shelf regions. The depth profile indicates an increase to a mid-water maximum of about 3 Bq/m³ and the decreasing again to lower levels at greater depths (Fowler, 2011).

Po-210 can accumulate in various environmental materials such as biota, sediments, etc. which is strongly accumulated in a variety of marine organisms (Cherry and Shannon, 1974). Therefore, it can be of great concern from the standpoint of radiation protection because of its radio-toxicity. Po-210 is known to be a major contributor to the natural radiation dose received by these organisms (Cherry and Heyraud, 1988) and critical group doses in particular seafood consumption (CEC, 1990). The concentration of Po-210 in edibles of marine organisms is very much higher than that of seawater because of biological re-concentration processes (Musthafa and Krishnamoorthy, 2012). Due to the even activity concentration in ocean water, the concentrations of Po-210 in marine biota are related to species rather than to geographical regions. Typical activity concentration values for species within the larger groups of fish are in the order of 2.4 Bq/kg (wet weight), for mollusks and crustacean the corresponding values of Po-210 concentrations are 15 Bq/kg (wet weight) and 6 Bq/kg (wet weight), respectively (Aarkrog et al., 1997).

Radionuclides such as Po-210 can be transported from the water to the sediment phases by physical (e.g. sedimentation), chemical (e.g. ion-exchange, polymerisation, colloid aggregation) and biological (e.g. detris) processes. Physical remobilization of contaminants from sediments to water can occur due to natural or anthropogenic re-suspension of the sediments, e.g. during flooding, erosion or estuary dredging; chemical mobilisation includes ion-exchange, leaching, and dissolution. Biological processes can affect both chemical and physical mobilisation (eg. bioturbation) (Rudjord et al., 2019). In other words, sediment is the primary repository of radionuclides and chemicals in the marine environment and it is a major indicator for chemicals pollution and radionuclides deposition such as for strong particle reactive of Po-210. Thus, marine sediments are commonly used as environmental matrices in chemical and radioactive monitoring programs (Saçan et al., 2010).

Therefore, the data presented are a part of the IAEA CRP K41017 project which has performed from 2017 to 2021. The main objectives of the current study are to quantify the radioactivity and assess the value of CF and K_d of Po-210 in seawater, biota and sediment from the surrounding area of Pantai Melawi, Tok Bali and Pulau Perhentian.

MATERIALS AND METHODS

Sampling

Sampling was conducted at five sampling stations in surrounding of Pantai Melawi (ML01), Tok Bali (TB01 and TB03) and Pulau Perhentian (PP02 and PP04) area are shown in Figure 1 and their sampling details are summarized in Table 1. 20 L of surface seawater sample (0.5 m) was collected at each sampling station using in-house modified water bottle sampler, while sediment samples were collected using surface Ponar grab sampler and biota samples were collected by manually fishing and purchased from local fisherman.

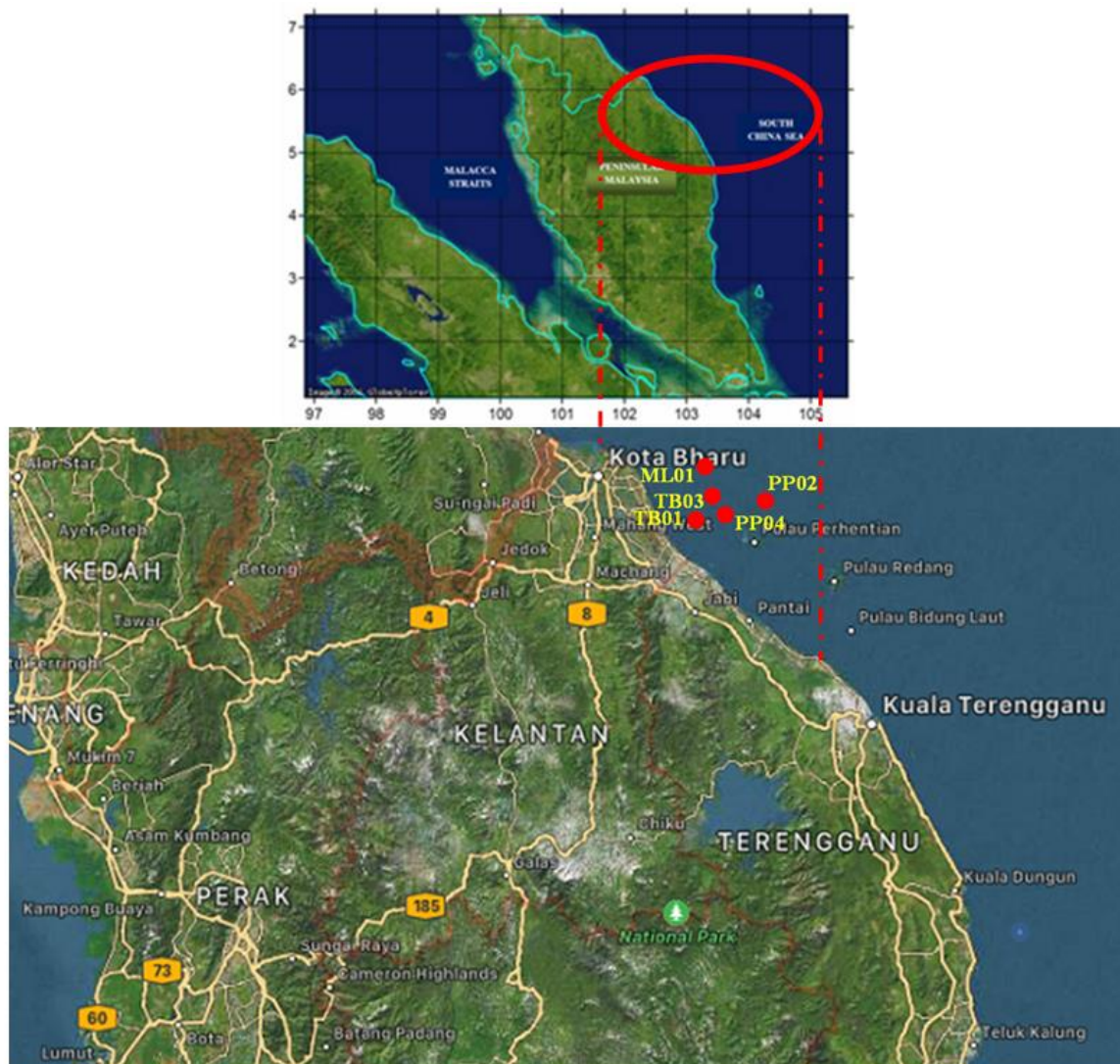


Figure1: Map showing the sampling point at the east coast of Peninsular Malaysia

Table 1: Detail of sampling location and seawater data

Location	Sampling Point	Coordinate		Sampling Date	Water Depth (m)	Salinity (ppm)	pH	Temperature (°C)
		Latitude, N	Longitude, E					
Pantai Melawi	ML01	06° 05.151'	102° 34.468'	23 Sept. 2017	22.1	31.0	7.2	29.7
Tok Bali	TB01	05° 56.847'	102° 32.543'	23 March 2018	15.5	32.0	6.4	26.0
	TB03	05° 58.067'	102° 35.657'	05 May 2018	23.0	32.4	7.0	30.4
Pulau Perhentian	PP02	05° 59.562'	102° 45.227'	04 May 2018	35.4	32.3	6.9	32.0
	PP04	05° 56.659'	102° 37.848'	05 May 2018	25.7	32.4	6.9	30.2

Sample Pre-treatment

The sediment and biota samples were weighed for fresh/wet weight and were then oven-dried at temperature approximately 80°C for 2 – 4 days or until reach to constant weight. Then, the dried samples were crushed and homogenized.

Sample Preparation and Digestion

For sediment samples: 1 mL of a known activity concentration of Po-209 tracer was added to 0.5 g of sediment sample and the sample was digested with a mixture of 15 mL of concentrated HF, 10 mL of concentrated HNO₃, 5 mL concentrated HClO₄ and 1 mL of H₂O₂. The sample was evaporated on a hot plate until almost dryness and keeps cool. After that, 5 mL of concentrated HNO₃ and 1 mL of H₂O₂ were added into the samples and were evaporated again until almost dryness. 10 mL of concentrated HCl was further added into the sample then evaporated until almost dryness and the sample was let to cool.

For biota samples: 0.5 g of sample was spiked with 0.5 mL of a known activity concentration of Po-209 tracer and was digested by adding 10 mL of concentrated HNO₃ and was evaporated on a hot plate to dryness. Then, 10 mL of concentrated HNO₃ and 1 mL of H₂O₂ were added and evaporate to almost dryness. Finally, 10 mL of concentrated HCl was added into the samples, then evaporated until almost dryness and the sample was let to cool.

For seawater samples: 1 L of seawater was used for the analysis. The sample was acidified with 2 mL of concentrated HCl and 0.1 mL of a known activity concentration of Po-209 tracer was added into the sample. 0.5 mL of saturated KMnO₄ was added and the pH of the solution was adjusted to pH 8 – 9 by adding 10 M NaOH. After that, 10 mL of 0.5 M MnCl₂ was added into the beaker and the solution was stirred for 3 hours and left overnight. The supernatant was decanted, centrifuged and the precipitate was rinsed until neutral pH obtained. Then, the precipitate was dissolved in a

small volume of concentrated HCl and H₂O₂ and evaporated until dryness. The dry residues were dissolved in 2 M HCl and proceed to radiochemical separation using Sr resin for the purpose of Pb-210 analysis.

Radiochemistry Separation

The dissolved precipitate of seawater in 2 M HCl was performed radiochemical separation using Sr resin. 0.7 g of Sr resin was loaded on a separation column with a ball of glass wool on top of the resin. Firstly, the resin was pre-conditioned by adding 10 mL of distilled water and 15 mL of 2 M HCl. Then, the dissolved precipitate was loaded into the Sr resin and was rinsed twice with 5 mL of 2 M HCl. Sr resin was further rinsed with 15 mL of 2 M HCl and the eluent was discarded. Po-210 was eluted by passing 25 mL of 6 M HNO₃ into the resin and the collected solution which contains polonium isotope was then evaporated to dryness.

Spontaneous Auto-deposition

3.3 mL of concentrated HCl was added to the dried sample until totally dissolved and dissolution. Then, the solution was transferred into the plating jar and added with distilled water until mark up of 80 mL. 1 mL of stable Bi carrier (10 mg/g) solution and 1 g of hydroxylammoniumchloride were added into the solution and was heated gently until all precipitate dissolve. Polished silver disks were mounted in the plating holder and were put slowly and carefully into plating jar to avoid the solutions are splashing out. The plating jars were placed on a magnetic stirrer hot plate, stirred and heated at a temperature of 85°C for four hours. After the plating process is completed, the plating holders were taken out, washed with distilled water and rinsed with ethanol. Lastly, the discs were air dried.

Counting by Alpha Spectrometry System

The measurement of Po-210 particles was carried out by using alpha spectrometry system (Ortec, Ortrate Plus) for 24 hours.

RESULTS AND DISCUSSION

Po-210 activity concentrations measured in seawater, biota and sediment samples are presented in Table 2. The highest activity concentration of Po-210 in seawater is recorded at TB03 with the value of 2.16 ± 0.09 Bq/m³, while the lowest found at PP04 with the value of 0.39 ± 0.02 Bq/m³. This indicated that Po-210 activity concentration in seawater samples ranged from 0.39 ± 0.02 Bq/m³ to 2.16 ± 0.09 Bq/m³. The results found that Po-210 in seawater taken from TB01 and TB03 located in the same near shore area were a significant difference. This could be assumed that decreased Po-210 concentration in TB01 due to dilution and flushed off by heavy rainfall before sampling and deep seawater reaches to the study location brought by strong waves during the sampling conducted. The results also found that Po-210 at surrounding of Pulau Perhentian (PP02 and PP04) was relatively lower than Tok Bali (TB03 and TB01) and Pantai Melawi (ML01). This due to Tok Bali and Pantai Melawi sampling point are located near to mainland (10 – 20 km) which was received more input of Po-210 from terrestrial compared to sampling point of Pulau Perhentian (> 30 km). However, this is contrary to other reports that the concentration of Po-210 on the coastal area is approximately the same as in the open sea since the main source of Po-210 in the seawater is from the atmospheric deposition.

Table 2: Po-210 activity concentrations in seawater, biota and sediment; and its CF and K_d values

Sampling Point	Po-210 Activity Conc. in Seawater (Bq/m ³)	Name of Fish	Habitat	Po-210 Activity Conc. in Fish (Bq/kg fw)	Po-210 Activity Conc. in Sediment (Bq/kg dw)	Concentration Factor, CF (L/kg)	Distribution Coefficient, K_d (L/kg)
ML01	1.84 ± 0.08	Ikan selar gelek / Yellowtail scad / <i>Atule mate</i>	Pelagic	50.13 ± 2.24	48.21 ± 2.15	2.73 x 10 ⁴	2.62 x 10 ⁴
		Ikan kunyit / Indian snapper / <i>Latjanus madras</i>	Demersal	4.06 ± 0.11		0.22 x 10 ⁴	
TB01	0.63 ± 0.03	Ikan selar gelek / Yellowtail scad / <i>Atule mate</i>	Pelagic	67.03 ± 3.00	69.14 ± 3.09	10.64 x 10 ⁴	10.97 x 10 ⁴
		Ikan kunyit / Indian snapper / <i>Latjanus madras</i>	Demersal	35.59 ± 1.59		5.65 x 10 ⁴	
TB03	2.16 ± 0.09	NS	-	-	35.86 ± 1.60	-	1.66 x 10 ⁴
PP02	0.43 ± 0.02	Ikan selar gelek / Yellowtail scad / <i>Atule mate</i>	Pelagic	34.07 ± 1.53	51.15 ± 2.29	7.92 x 10 ⁴	11.90 x 10 ⁴
PP04	0.39 ± 0.02	Ikan kekacang / Obtuse barracuda / <i>Sphyraena obtuse cuvier</i>	Pelagic	11.96 ± 0.54	51.58 ± 2.31	3.07 x 10 ⁴	13.23 x 10 ⁴
		Ikan kunyit / Indian snapper / <i>Latjanus madras</i>	Demersal	25.52 ± 1.14		6.54 x 10 ⁴	

NS: no sample

For the biota, activity concentrations of Po-210 were ranged of 4.06 ± 0.18 Bq/kg fw to 67.03 ± 3.00 Bq/kg fw which significantly higher value in pelagic fish i.e. Yellowtail scad (*Atule mate*). Since pelagic fish lives in the water column or the pelagic zone of the ocean, while demersal fish live and feed on the bottom of the sea. Thus, this related to the depth profile indicated an increase of Po-210 to a mid-water (Fowler, 2011) which almost pelagic fishes live in this zone and the decreasing again of Po-210 to lower levels at greater depths (Fowler, 2011) which demersal fish live and feed. This finding indicates that Po-210 in fishes is most probably contributed by the Po-210 in seawater and not from the sediments. Other than that, Po-210 also showed a higher affinity towards sediments compared to fishes. On the other hand, this variation of Po-210 activity concentrations may be because of the different habitat, location and feeding behavior of the species. It is strictly proven by Carvalho and Fowler (1993) that the ingestion of food also plays a major role in the accumulation of Po-210.

The activity concentrations of Po-210 in sediments were ranged of 35.86 ± 1.60 Bq/kg dw to 69.14 ± 3.09 Bq/kg dw. This indicated the highest value at TB01 and lowest at TB03, both points are in the same near-shore area but the different distance from the mainland. This variation could be explained that input of Po-210 from terrestrial was supplied to the study point via river and run-off water, as well as sediment/soil particle from soil erosion at the terrestrial area. According to IAEA (2017), the variation levels of Po-210 in sediment are affected by the change of redox condition of iron and manganese in the sediment. During the anoxic period, the level of Po-210 can be significantly increased.

Concentration Factor (CF) is understood as the concentration ratio of a contaminant substance in biota and the concentration of the same substance in surrounding water were first introduced in aquatic toxicology (Rand, 1995). This factor is usually represented in terms of an activity concentration in biota relative to that in ambient seawater (IAEA, 2004). Then, $CF (L/kg) = \text{Concentration per unit mass of the organism (Bq/kg fresh weight)} / \text{Concentration per unit mass of seawater (Bq/L)}$. Meanwhile, the distribution coefficient (K_d) is the basic parameter used to determine the degree of radionuclides sorption on solids and characterize the mobility of radionuclides in the environment. It is also one of the major parameters determining the fate of radionuclides in the environment. Therefore, $K_d (L/kg) = \text{Activity concentration per unit mass of solid phase (eg. sediment) (Bq/kg dry weight)} / \text{Activity concentration per unit mass of aqueous phase (eg. seawater) (Bq/L)}$. The results of the CF were ranged of 2.73×10^4 L/kg to 10.64×10^4 L/kg for pelagic fish and 0.22×10^4 L/kg to 6.54×10^4 L/kg for demersal fish. This indicated CF of Po-210 for pelagic fish was relatively high than demersal fish. In the case of the type of fish, both of pelagic and demersal fishes observed CF values were higher than the values published by the IAEA (1985), Lubna et al. (2011) and Mohamed et al. (2006). This may probably depend on the factors of the physical and chemical properties of the ambient water, behaviour of fishes and related to their species; and geographical regions.

For the K_d values found to be varied with the ranges of 1.66×10^4 L/kg to 13.23×10^4 L/kg, this showed that TB03 with the lowest and PP04 with the highest value of K_d for Po-210. This variation of K_d values for Po-210 most probably due to the sediment particle size, where PP04 covered by fine particle sediment (silt: 40.22% and clay: 2.12%) compared to TB03 which are contained 13.23% of silt and 0.36% of clay. Furthermore, this indicated that Po-210 in this PP04 area is probably highly bounded and sorption of Po-210 to solid i.e. sediment, thus resulting in a lower activity concentration in seawater. The higher K_d means the greater of the Po-210 proportion in the sediments. It follows that the mobility of Po-210 in a water-sediment system will be limited by the strength of sorption to the sediment, the reversibility of the sorption mechanism and the kinetics of

the sorption/desorption processes. These factors will in turn depend upon the physical and chemical properties of the radionuclide i.e. Po-210, the water and the sediment (Rudjord et al., 2019).

CONCLUSION

Generally, Po-210 activity concentration is found to be the highest at sampling point nearest to the coastal area that received more input of Po-210 source from the terrestrial. This result is also probably due to the sea condition during sampling which might changes in Po-210 activity concentration. Pelagic fishes have higher activity concentration of Po-210 compared to demersal fishes. These variations of Po-210 activity concentrations may be because of the different habitat and species, location and feeding behavior of the fishes. The variation levels of Po-210 in sediment are probably affected by the change of redox condition of iron and manganese in the sediment. During the anoxic period, the level of ^{210}Po in sediment can be significantly increased. The results of the study indicated CF of Po-210 for pelagic fish was relatively high than demersal fish, probably depends on the factors of the physical and chemical properties of the ambient water, behaviour of fishes and related to their species; and geographical regions. Meanwhile, the variation of K_d values for Po-210 most probably due to the sediment particle size.

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