Natural Radium Detection and Inventory Flux of Isotopes in Particulate and Dissolved Phases of Seawater at Kapar Coastal Area Caused by Coal-Fired Power Plant

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Abstract. Distribution of ²²⁶Ra and ²²⁸Ra radioactive in marine have been studied at Kapar coastal area that closed to Sultan Salahudin Abdul Aziz Shah (SJSSAS) power station. The concentration level of ²²⁶Ra and ²²⁸Ra were measured in seawater include total suspended solids (TSSₚₑₜ) and dissolved phases from September 2006 to February 2008. The measurement technique used for ²²⁶Ra and ²²⁸Ra was using cation exchange column and counted using Liquid Scintillator Counter (LSC). The radioactivities of ²²⁶Raₑₜ and ²²⁸Raₑₜ in the dissolved phase of seawater ranged from 1.29 ± 0.52 mBq/L – 3.69 ± 1.29 mBq/L and 2.12 ± 0.71 mBq/L – 17.07 ± 6.03 mBq/L respectively. The measurement of radioactivities of radium isotopes in the particulate phase of seawater ranged from 15.62 ± 1.99 Bq/kg – 241.76 ± 100.23 Bq/kg (²²⁶Raₑₚₑₜ) and 7.19 ± 3.21 Bq/kg – 879.66 ± 365.74 Bq/kg (²²⁸Raₑₚₑₜ). Radium isotopes inventory in this study showed that suspended solid have higher inventory value than seawater and sediment. Study also found that suspended solid play an important role for flux contribution at seawater. Based on the finding, the radioactivity concentration of ²²⁶Ra and ²²⁸Ra is higher in particulate phase than in dissolved phase.

Keywords: Radium, coal-fired, seawater.

1. Introduction

Industrial revolution has introduced coal as crucial global energy sources. Coal is the world’s most abundant and accessible source of fossil energy. It is also believed that coal is a source in circulation pattern of environmental marine of coal power station where natural radionuclide such as radium isotopes associated with coal [1]. Radium isotopes, ²²⁶Ra (T₁/₂ = 1600 years) and ²²⁸Ra (T₁/₂ = 5.75 years) are affected by vertical mixing, horizontal circulation and adsorption from particulate in seawater. ²²⁶Ra and ²²⁸Ra are among the most important isotopes in the environment from radio protection points of view. ²²⁶Ra is powerful tool for studying geo-hydrological processes. It is used intensively as tracers for tracking groundwater sources that discharge into the coastal ocean [2,3,4] and mixing processes between the coastal zone and open ocean [5].

Inventory is a parameter that used to estimate and evaluate the incremental transfer/accumulation of element such as radionuclides, metals and others that mainly occur in
seawater sediments. Inventory of radionuclides in sediment is measured by measuring the radioactivity of radionuclide in the sediment by using following equation [6,7]:

\[
I (\text{Bq/m}^2) = \text{Radioactivity (Bq/m}^3) \times \text{Average depth (m)}
\]  

(1)

Flux is a parameter used for assessing the rate or velocity/collection of elements in a dissolved substances, suspended matter and sediments by dividing inventory with time of sampling. Equation used to estimate radionuclide flux is based on equation as follow:

\[
F = I \lambda
\]  

(2)

Where

\[
F=\text{flux},\]
\[
I=\text{inventory},\]
\[
\lambda=\text{constant value}
\]

Since the study on \(^{228}\text{Ra}\) and \(^{226}\text{Ra}\) as geochemical tracer in marine are poorly known in Malaysia, this study carried out to observe the distribution of radium isotopes in marine phases at Kapar coal-fired power plant. The main aims of this study are to determine the concentration of radium isotopes and flux in three different phases of seawater at Kapar coastal area.

2. Materials and Methods

2.1 Study Area
Kapar Coal-fired Powerplant known as Sultan Salahudin Abdul Aziz Powerplant (SSAAPP) is one of the largest electric coal powerplants in Malaysia with capacity of 2420 MW and produced 23% energy at the maximum demand (TNB 2014). It was opened in March 1987 and the only power station in Malaysia with triple fuel firing capability which is gas, oil and coal. The study station is located by seaside near Kapar in Klang (Table 1).

| Site | Station | Latitude | Longitude |
|------|---------|----------|-----------|
| Kapar Coastal | 1 | 03° 5' 55.4" | 101° 17' 59.7" |
| | 2 | 03° 7' 25.8" | 101° 18' 1.8" |
| | 3 | 03° 6' 37.2" | 101° 08' 40.4" |
| | 4 | 03° 5' 53.0" | 101° 19' 18.6" |
| | 5 | 03° 6' 27.1" | 101° 19' 43.8" |
| | 6 | 03° 5' 55.4" | 101° 17' 59.7" |
2.2 Methods
Six stations of seawater samples were collected from coastal area of Kapar power plant. Seawater samples were filtered through 0.45µm pore size of pre-weighed membrane filter paper. Seawater samples were acidified with concentrated HNO$_3$ to pH 2. Then, 1 ml of barium and carrier solutions (25mg/l) and Na$_2$CO$_3$ was added into the samples. Ammonia solutions were added continuously to the samples and were stirred vigorously until pH 10. After supernatant appear, siphon out the supernatant from the filtrate, and dissolve the carbonate with HNO$_3$ and HClO$_4$. Centrifuged was used to remove supernatant and then dissolved in 20 ml of 1% HClO$_4$ and stand in warm for 1-2 hours.

For particulate phases (total suspended solid and sediment) were weighted after dried into the oven at 70ºC. 1 ml of barium carrier (25mg/ml) was added into each sample into the Teflon beaker. Then the samples were evaporating to dryness with mixture consisting 10 ml of HNO$_3$, 5 ml of HClO$_4$ and 1 ml of HF on the hot plate. A few millimeters (0.5ml) of H$_2$O$_2$ were added at digestion stage. Then the residues were dissolved in 5 ml of concentrated HNO$_3$ and 1ml of HClO$_4$ and stand in warm condition.

After dissolved and particulate phases done, the samples were purified using the cation exchange column. 200 ml of 2M HCl were used to elute Ba (Ra) from the cation resin and dry the Ba (Ra) aqueous on the hotplate until dryness. Then, 20 ml of 0.5M HCl and 1 ml of H$_2$SO$_4$ were added into the residue until white Ba (Ra) SO$_4$ precipitate appeared. Milipore filter (25mm diameter, 0.45µm pore size) was used to filter the precipitate.

Then, dried and weighed to calculate the chemical yield. The precipitates together with filter paper were transferred into a 20 ml glass vial followed by adding Instagel® XF and Ultimate™ Gold AB. The vials stored for over 21 days after well mixing using ultrasonic cleaner [8,9,10]. The vials were counted using liquid scintillation counter (LSC).

3. Results and Discussion
3.1 Distribution of $^{228}$Ra and $^{226}$Ra in dissolved, total suspended solids and sediment in seawater
The activity of $^{226}$Ra and $^{228}$Ra concentration in dissolved varied widely from 1.41 mBq/L to 3.69 mBq/L and 6.01 mBq/L to 17.07 mBq/L respectively. The activities of $^{228}$Ra concentration in Kapar coastal area have been found relatively low level and almost similar than other surface area samples elsewhere in Malacca Straits [11,12] and world oceans. Mean concentration of $^{226}$Ra and $^{228}$Ra is differing for each sampling time.
ANOVA analysis showed significant difference 95% confidence for $^{228}\text{Ra}$ ($p=0.000$) and $^{226}\text{Ra}$ ($p=0.001$) with different sampling location for dissolved phase. Pearson correlation analysis showed a strong negative correlated between mean of radium activity and sampling occasions at Kapar ($r =0.741$) for $^{228}\text{Ra}$. This is probably due to high dilution from different source (Figure 2).

### Table 2. Mean radioactivity of $^{226}\text{Ra}_{\text{sw}}$ and $^{228}\text{Ra}_{\text{sw}}$ at Kapar coastal area.

| Time | $^{226}\text{Ra}$ (mBq/L±1 σ) | $^{228}\text{Ra}$ (mBq/L±1 σ) |
|------|-------------------------------|-------------------------------|
| Mar 07 | 2.34 ± 0.91                  | 11.02 ± 4.44                  |
| Aug 07 | 1.65 ± 0.59                  | 8.08 ± 3.33                  |
| Nov 07 | 1.86 ± 0.64                  | 7.67 ± 3.07                  |
| Feb 08 | 1.55 ± 0.59                  | 7.44 ± 2.92                  |

**Figure 2.** relationship between radium isotopes and sampling occasions in dissolved phase in seawater (mean values of four times sampling).

Radium isotopes activity in total suspended solids in seawater ($\text{TSS}_{\text{sw}}$) was higher than dissolved phase with mean activity of $^{228}\text{Ra}$ in $\text{TSS}_{\text{sw}}$ range from $17.73\pm6.33\text{Bq/kg}$-$879.66\pm365.74\text{Bq/kg}$. Meanwhile for $^{226}\text{Ra}$ in $\text{TSS}_{\text{sw}}$ range from $5.62\pm1.99\text{Bq/kg}$ – $241.76\pm100.23\text{Bq/kg}$.

In total suspended solids ($\text{TSS}_{\text{sw}}$) phase, radium isotopes activities was varied based on its sampling location. This was supported by ANOVA result that found significant 95% confidence level $p=0.002$ for $^{226}\text{Ra}$ and $p=0.003$ for $^{228}\text{Ra}$ (Figure 4). $^{228}\text{Ra}$ and $^{226}\text{Ra}$ activity in particulate phases were varied from 3.15 to 4.83. It found that $^{228}\text{Ra}$ are more abundance than $^{226}\text{Ra}$ in dissolved phase. It also found that most of the sampling stations showed high activity values of $^{226}\text{Ra}$/$^{228}\text{Ra}$. It may due to enrichment of $^{228}\text{Ra}$ in removal of $^{228}\text{Ra}$ from water column onto the particles which is caused from coal burning operation of Kapar power station.

### 3.2 Inventory and flux of $^{226}\text{Ra}$ and $^{228}\text{Ra}$ at Sultan Salahudin Abdul Aziz Power Plant coastal area.

Inventory of $^{226}\text{Ra}$ showed value range from $2.53 \times 10^3$ Bq / m$^2$ - $3.63 \times 10^3$ Bq / m$^2$ (March 2007), $2.59 \times 10^3$ Bq / m$^2$ - $3.62 \times 10^3$ Bq / m$^2$ (August 2007), $1.56 \times 10^3$ Bq / m$^2$ - $1.74 \times 10^3$ Bq / m$^2$ (November 2007) and $1.61 \times 10^3$ Bq / m$^2$ - $2.52 \times 10^3$ Bq / m$^2$ (February 2008). It was found that at the time of sampling in November and February showed a low inventory as both the months was dry season (northeast monsoon). Flux also showed inconsistencies as inventories as the flux value changed based on the sampling location.
Figure 3. Distribution of \(^{226}\text{Ra}_{\text{sed}}\) and \(^{228}\text{Ra}_{\text{sed}}\) radioactivity at Kapar coastal area.

Figure 4. Relationship between radium isotopes and sampling occasions in total suspended solids (TTS\(_{\text{SW}}\)) phase in seawater (mean values of four sampling).
The average flux of sediment in the range of $6.78 \times 10^3$ Bqm$^{-2}$ yr$^{-1}$ to $7.13 \times 10^3$ Bqm$^{-2}$ yr$^{-1}$ for $^{226}$Ra$_{sed}$ and $28.01 \times 10^3$ Bqm$^{-2}$ yr$^{-1}$ to $55.49 \times 10^3$ Bqm$^{-2}$ yr$^{-1}$ for $^{226}$Ra$_{sed}$ (Table 3). ANOVA analysis showed a significant difference between the inventory and the flux at the 95% significance level in all research stations with $p = 0.000$.

First sampling recorded highest inventory and fluxes in radium isotopes. It may explained that the time and location of sampling not only active with the biological activities but also active with physical activities such as flow and water flow, wave, tidal, and wave which accelerates the transport of biological accumulation elements to the area [7].

Resulted from three sampling phase showed that inventory is in order of suspended solid > Sediment > Seawater. Suspended solid phase capable of trapping and adsorb the chemicals in the water column [13]. The content of suspended particulate matter in the estuary has always been high and is constantly changing depending on the tide and are affected by the wind. This situation will result in an inventory of the sediment surface higher than the inventory in seawater.

Total radium isotopes flux in seawater and suspended solid recorded high value of during February for $^{226}$Ra is $17.21 \times 10^4$ Bq/m$^2$/yr and $67.82 \times 10^5$ Bq/m$^2$/yr for $^{228}$Ra. Study found that total flux for $^{228}$Ra is higher than $^{226}$Ra. This is caused gap in half-life of both isotopes which $^{226}$Ra is 1602 and 5.75 years for $^{228}$Ra. Studies conducted by Phuah et al., [9] found that the amount of suspended material plays a crucial factor for contribution of flux in Straits of Malacca (West Coast) or South China Sea (East Coast). The values of radium isotopes flux from total suspended solid was higher than others samples. It believed that particles play an important role in a source of radium isotopes in estuaries or sea.

### Table 3. Radium isotopes flux at Kapar coastal area.

| Sample type | March 2007 | August 2007 | November 2007 | February 2008 |
|-------------|------------|-------------|---------------|---------------|
|             | $^{226}$Ra | $^{228}$Ra | $^{226}$Ra | $^{228}$Ra |
| Seawater    | 35.71      | 194.39      | 27.87         | 87.89         |
|             | $^{226}$Ra | $^{228}$Ra | $^{226}$Ra | $^{228}$Ra |
| Suspended solid | 2.18 x $10^3$ | 2.22 x $10^4$ | 10$^3$ | 9.11 x $10^4$ |
|             | 55.49 x $10^3$ | 50.57 x $10^3$ | 32.87 x $10^3$ | 6.50 x $10^3$ |
| Sediment    | 13.07 x $10^3$ | 10$^3$ | 10.92 x $10^3$ | 6.78 x $10^3$ |
| Total       | $6.10 \times 10^4$ | $27.37 \times 10^4$ | $27.27 \times 10^4$ | $37.10 \times 10^5$ |

### 4. Conclusions

Highest values of radium were detected at total suspended solids compared with dissolve phase in seawater. Radium isotopes inventory and flux were varied based on sampling location and monsoon season. Isotopes inventory show in order of Suspended solid > Sediment > Seawater. The mean concentrations of flux for one year are $9.34x10^4$ for $^{226}$Ra and $3.99x10^6$ for $^{228}$Ra.

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