EnvironmentAsia
The international journal published by the Thai Society of Higher Education Institutes on Environment

Available online at www.tshe.org/EA
EnvironmentAsia 3(2) (2010) 97-108

Natural Radium Isotopes in Particulate and Dissolved Phases of Seawater and Rainwater at the West Coast Peninsular Malaysia Caused by Coal-Fired Power Plant

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Abstract

The concentration levels of natural radium isotopes such as ^{226}Ra and ^{228}Ra were measured in the atmospheric samples including rainwater, total suspended solids (TSS_{rw}) and marine environment samples collected around the Kapar coal-fired power plant from September 2006 to February 2008. Activity concentration of ^{228}Ra and ^{226}Ra in rainwater showed the higher concentrations compared to the seawater. The mean activities of ^{226}Ra and ^{228}Ra in rainwater at Kapar were 20.45±4.50 mBq/L and 74.82±25.38 mBq/L, respectively. Meanwhile the levels in total suspended solids (TSS_{rw}) of rainwater showed 226.99±52.57 Bq/kg for ^{226}Ra and 439.92±186.17 Bq/kg for ^{228}Ra. The measurements of radium isotopes concentration in rainwater at coal-fired power plant in Kapar are found in relation to their sources and application as tracers in lower atmosphere. The mean value of pH in rainwater during this study is pH 5.51 slightly acidic as lowest value for the standard of clean rainwater. Radium in seawater also strong adsorption onto total suspended solids with the distribution coefficient, Kd values of ^{228}Ra and ^{226}Ra ranged from 0.054×10^4 to 163.90×10^4 L/g and between 0.49×10^4 to 191.54×10^4 L/g, respectively.

Keywords: radium; coal-fired; seawater; rainwater; distribution coefficient

1. Introduction

Nowadays, industrial revolution brought coal to the fore front of global energy scene. Coal is the world's most abundant, most accessible and most versatile source of fossil energy. It also widely believed as a source in circulation pattern of aerosol in the atmosphere and environmental marine of coal power station where natural radionuclide such as radium isotopes associated with coal (Cevik *et al*., 2007). The concentration of radionuclide in precipitation as a function of many factors including the radionuclide concentration and spatial distribution in air column such as; aerosol particle size distribution, size and phase of the hydrometer (e.g., raindrop or snow), how they was predominantly captured by precipitation (below the cloud or within the cloud), degree of evaporation prior to reaching the earth surface and duration of precipitation event (Martin, 2003).

Once in the atmosphere, these pollutants undergo chemical and physical transformation through complex atmospheric processes to form secondary pollutants as particulates or aerosols (Polkowska *et al*., 2005). The nature of these pollutants and meteorological conditions influence the way atmospheric pollutants are eventually sequestered via wet or dry deposition (Baez *et al*., 2007); some are deposited close to the source while others are transported over longer distances before being deposited (Hedge *et al*., 2007) onto surfaces. The chemical composition of atmospheric deposition, therefore, is a signature of several interacting physical and chemical processes including emission and sources; transport and dynamics of the atmosphere; and removal processes involved. The effects of atmospheric deposition include acidification of lakes and streams, nutrient enrichment of coastal waters and large river basins, soil nutrient depletion and decline of sensitive forests, agricultural crop damage, and impacts on ecosystem biodiversity (Polkowska *et al*., 2005, Zhao *et al*., 2008).

Mining, milling, transporting and production of coal are ways of exposing the workers, public and the environment to enhanced natural radioactivity (UNSCEAR, 1993; Horton *et al*., 1988; IAEA, 2004). Radium emitted into the atmosphere from phosphate rocks, burning coal and phosphate fertilizer waste materials decays to their daughters, e.g., ^{210}Pb. Dispersion of coal are throughout from the chimney is blow by the wind and rainwater will attach to the surface of pre-existing aerosols and released as a dust or fly ash was transported by rainwater in the area radius at coal power plant.

Radium isotopes, ^{226}Ra ($T_{1/2}$ = 1600 years) and ^{228}Ra ($T_{1/2}$ = 5.75 years) are affected not only by vertical mixing and horizontal circulation but also the adsorption from particulate in rainwater and seawater. ^{226}Ra and ^{228}Ra are among the most important isotopes in the environment from radio protection points of view. ^{226}Ra is powerful tool for studying geo-hydrological processes. It is used intensively as tracers for tracking groundwater sources that discharge into the coastal ocean (Moore 1996, Charette *et al.*, 2001, Burnett and Dulaiova, 2003) and mixing processes between the coastal zone and open ocean (Moore, 2000).

Collaboration water with other *in-situ* parameters such as chlorine, pH and temperatures are giving an idea focused in this study. Exposure to chlorine can occur in the workplace or in the environment following releases to air, water, or land. Chlorine is generally found only in industrial settings. Water and wastewater treatment plants use chlorine to reduce water levels of microorganisms that can spread disease to humans (disinfection). Chlorine dissolves when mixed with water. It can also escape from water and enter air under certain conditions. Most direct releases of chlorine to the environment are through air and surface water. Once in air or in water, chlorine reacts with other chemicals. It combines with inorganic material in water to form chloride salts, and with organic material in water to form chlorinated organic chemicals.

Studies on ^{228}Ra and ^{226}Ra as geochemical tracer in marine and atmosphere environments are poorly known in Malaysia. Thus, the aim of this study is to observe the distribution of radium isotopes in marine and atmospheric phases at Kapar coal-fired power plant.

2. Materials and Methods

2.1. Study area

Kapar Coal-fired Power Plant known as Sultan Salahudin Abdul Aziz Power Plant (SSAAPP) is one of the largest electric coal power plants in Malaysia which is the capacity about 2420 MW and produced 23% energy at maximum demand (TNB 2003) which is built near seasides and riversides of Malacca Straits. Mangrove forest is a key feature of the coastline where the power plant is located. The station is located by seaside near Kapar in Klang, Selangor (Fig. 1). The SSAAPP was opened in March 1987 and lies between the mouths of Kapar Besar and Serdang Kecil rivers (Table 1).

2.2. Methods

2.2.1. Dissolved, and particulate phases

About six stations of seawater and rainwater samples were collected from the coastal area of Kapar power plant (Figs. 1-2), where the *in-situ* parameters such as salinity, specific conductivity, pH and dissolved oxygen (DO) were also measured using the calibrated portable meter (Model: YSI-SCT 6810). After that, the rainwater and seawater samples were filtered through the 0.45 µm pore size of pre-weighed membrane filter paper. The seawater samples were acidified with concentrated HNO_3 to pH 2. Then, about 1 ml of barium and ferum carrier solutions (25 mg/ml) and Na_2CO_3 added into the samples. Samples were stirred vigorously after added ammonia solution and continued adding until pH 10. The supernatant will appeared and then siphon out the

Table 1. Sampling station codes at Kapar coastal water

Site	Station	Location	Latitude	Longitude
Coastal	1	saline	3° 5' 55.4" N	101° 17' 59.7" E
	2	saline	3° 7' 25.8" N	101° 18' 1.8" E
	3	saline	3° 6' 37.2" N	101° 08' 40.4" E
	4	saline	3° 5' 53.0" N	101° 19' 18.6" E
	5	brackish	3° 6' 27.1" N	101° 19' 43.8" E
	6	freshwater	3° 7' 3.10" N	101° 19' 48.7" E
Around coal-fired plant	A	G-1	3° 6' 50" N	101° 19' 17" E
	B	G-2	3° 6' 51" N	101° 19' 25" E
	C	C-1	3° 7' 04" N	101° 19' 32" E
	D	C-2	3° 7' 06" N	101° 19' 09" E
	E	C-3	3° 7' 19" N	101° 19' 08" E
	F	C-4	3° 6' 50" N	101° 19' 07" E

*G = from gas chimney
*C = from coal chimney

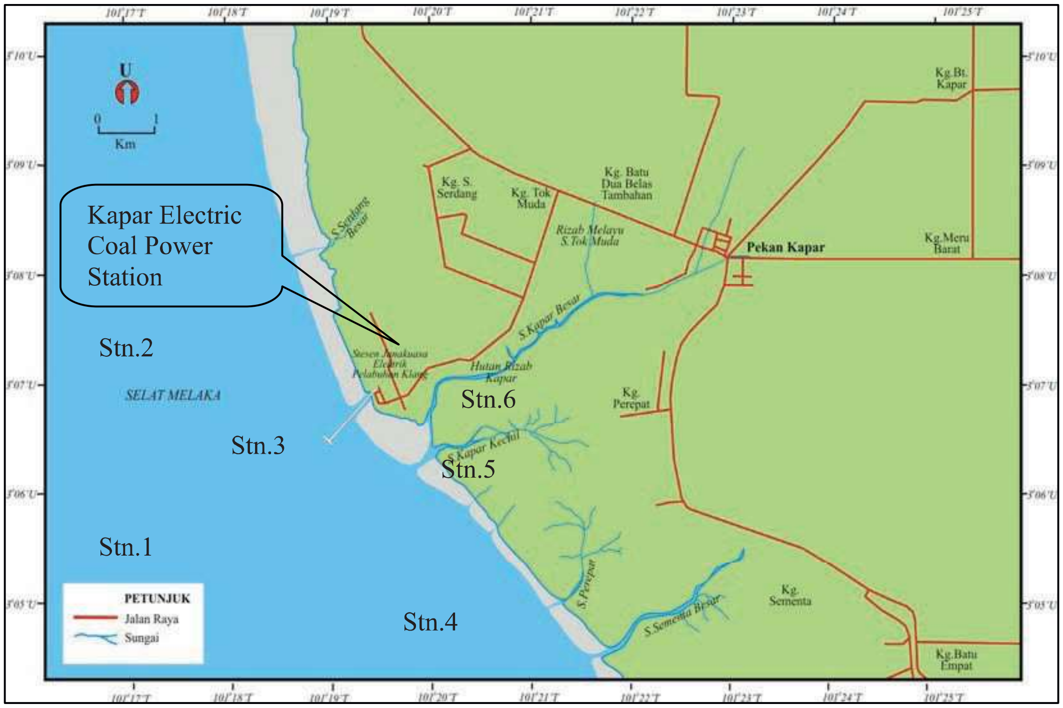


Figure 1. Location of study site and sampling area

supernatant from the filtrate, and dissolve the carbonate precipitate with HNO_3 and $HClO_4$. The supernatant was removed by centrifuged and dissolved in 20 ml of 1% perchloric acid and stand in warm for 1-2 hours.

The particulates phases such as total suspended solids were weighed after dried into the oven with temperature at 70^{o}C. About 1 ml of barium carrier (25 mg/ml) was added into each sample into the teflon beaker. The samples were evaporating to dryness with mixture acid consisting 10 ml of HNO_3, 10 ml of $HClO_4$ and 10 ml of HF on the hot plate. A few milliliters of H_2O_2 were adding during the digestion. The residues were dissolve in 10 ml of concentrated HNO_3 and 5 ml of HF, and stand in warm condition.

After finish the above steps (dissolved and particulate phases), the samples were purified using the cation exchange column. About 200 ml of 2M HCl were use to elute Ba(Ra) from the cation resin and dry the Ba(Ra) aqueous on the hotplate until dryness. About 20 ml of 0.5M HCl and 1 ml of H_2SO_4 were added into the residue until white $Ba(Ra)SO_4$ precipitate appeared. The precipitate was filtered by Millipore filter (25 mm diameter, 0.45 µm pore size), dried and weighed to calculate the chemical yield. The precipitates together with the filter paper were then transferred into a 20 ml glass vial followed by adding Instagel® XF and Ultimate™ Gold AB. After well mixing using ultrasonic cleaner, the vials stored for over 21 days or after the growth of the progeny nuclides (Chalupnik & Lebecka, 1990, 1993, Kim *et al*., 2001). The vials were counted using liquid scintillation counter (LSC).

3. Results and Discussion

3.1. Distribution of ^{228}*Ra and* ^{226}*Ra in dissolved and total suspended solids in seawater*

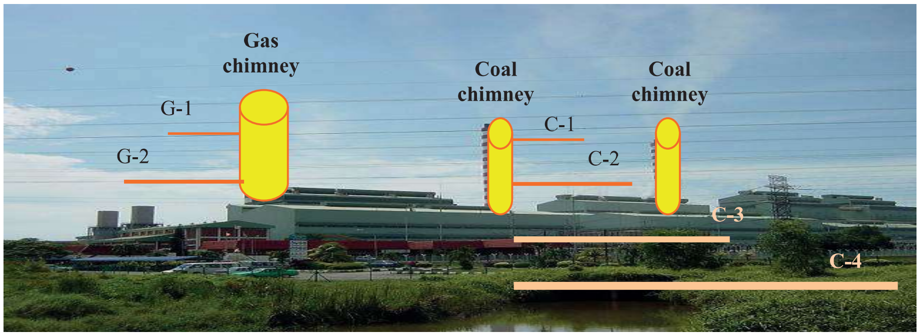


Figure 2. Location of sampling station in Kapar Coal-fired Power Plant

Measurements of ^{228}Ra and ^{226}Ra in samples taken from Kapar coastal water which is nearby Kapar power plant (coal burning area) in dry seasons (March 2007 and August 2007) and wet seasons (November 2007 and February 2008) are listed in Table 2. The seawater samples are approximately neutral, ranging from pH 6.72 to 8.90. Salinity and chlorine are symbiosis with each other. The value of chlorine ranged from 0.88 psu to 17.11 psu were calculated from Pilson *et al*., (1998) using 35 psu in seawater for salinity value. Additionally, the mean of Br/Cl and SO_4/Cl ratios in the water samples are 0.003 and 0.140, respectively. It is generally considered that a Br/Cl ratio in water retains that original source because little fractionation between Cl$^-$ and Br$^-$ occurs through geochemical process. If the origin of the water samples is derived from seawater, their ratios values should be similar to that seawater 0.0035 for Br/Cl.

The SO_4/Cl ratios in almost all the seawater were higher than river indicating the reduction of sulphate probably by bacteria (Yamanaka and Kumagai, 2006). The low salinity or Cl and Ra activities in river samples result from a nearly complete flushing from the river flood water (Breier *et al*., 2007). From the Cl results are increasing every sampling occasion in Kapar River with fluctuate in every sampling in seawater at Kapar coastal water.

In station 2, which placed a hot water give a higher temperature and Cl. In Kapar coastal water, the most significant differences in pH or Cl and radium activities between the sampling periods are associated with seasonal changes. In station 6, the Cl increasing in every sampling occasions ranged from 0.88 to 4.46 besides the ^{226}Ra and ^{228}Ra activities results are shown in Table 2.

In this study the seawater temperature (°C) were ranged from 29.5°C to 35.5°C which are listed in Table 2. The activity of ^{226}Ra and ^{228}Ra 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. In west coast of Peninsular Malaysia, the activities of ^{226}Ra concentration of most seawater in this study have been found at relatively low level and almost similar than other surface area sampled elsewhere in the Malacca Straits, (e.g., Nioo *et al*. (2005), Phuah *et al*. (2004) and Nozaki *et al*. (1998) and world oceans are listed in Table 3.

Dissolved phase was varied depend on the sampling location and it was proven by an ANOVA analysis that have significant difference 95% confidence for ^{228}Ra (*p=0.000*) and ^{226}Ra (*p=0.001*). The statistical correlation between mean of radium activity and sampling occasions at Kapar found a strong negative correlated using Pearson method (*r=0.741*) for ^{228}Ra was probably due to high dilution from different source (Fig. 3).

Reflecting the wide variation in ^{228}Ra, the seasonal change in the ^{228}Ra/^{226}Ra ratio mainly results from the change in ^{228}Ra activity. The ^{228}Ra/^{226}Ra ratio of dissolved phase of seawater from Kapar coastal water exhibited seasonal variation, minimum values observed during dry season (^{228}Ra/^{226}Ra = 2.67 – 4.99) and maximum values during wet season (^{228}Ra/^{226}Ra = 3.39 – 6.19).

Activity of radium isotopes in total suspended solids of seawater (TSS_{sw}) was slightly higher than dissolved phase, where the mean activity of ^{228}Ra in TSS_{sw} during dry season (156 Bq/kg) and (370 Bq/kg) during wet season (Table 2). Meanwhile, the mean activity of ^{226}Ra in total suspended solids (TSS_{sw}) phase is lower than ^{228}Ra activity, which is 35.63 Bq/kg for dry season and 95.95 Bq/kg for wet season. High activity ratio of ^{228}Ra/^{226}Ra might be imply that radium isotopes are derived from weathered materials, where most of mobile ^{228}Ra has already been lost during neap from dissolved phase and more attachable into the particulate phase. The removal of radium from dissolved to particulate phase at study sites probably related to the sortion/desorption process of ferum in the particulate matter.

Radium isotopes activities in total suspended solids (TSS_{sw}) phase was varied depend on the sampling location and it was proven by an ANOVA analysis found that significant 95% confidence level *p=0.002* or ^{226}Ra and *p=0.003* for ^{228}Ra (Fig. 4). The activity ratios of ^{228}Ra/^{226}Ra in the particulate phases were varied in the range of 3.15 to 4.83. Where the ^{228}Ra are more abundance in the dissolved phase and opposite shown by ^{226}Ra. Most of the sampling stations were found high activity values of ^{228}Ra/^{226}Ra ratio that indicating the enrichment of ^{228}Ra is likely due to relatively efficient removal of ^{228}Ra from water column onto the particles which is related to the coal burning operation by Kapar power station, and coal burning operation is one of the major source of natural radionuclides into environment.

The analysis of total suspended solids (TSS_{sw}) in the seawater at Kapar coastal water indicate that most of the radium was in solution but generally were

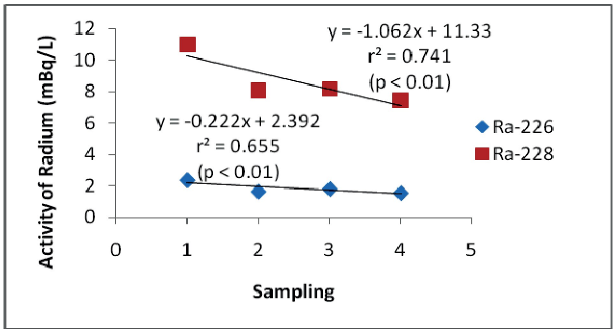


Figure 3. Relationship between radium isotopes and sampling occasions in dissolved phase in seawater (mean values of four times sampling)

Table 2. Activity concentration of ^{226}Ra and ^{228}Ra in the dissolved and total suspended solids (TSS_{sw}) in seawater

Sampling	Stn.	pH	S (ppt)	°C	$^{*}Cl^{-}$	^{228}Ra (mBq/L)	^{226}Ra (mBq/L)	^{228}Ra (Bq/kg)	^{226}Ra (Bq/kg)
Mar 2007	1	7.69	28.5	30.6	15.67	12.71 ± 5.01	2.75 ± 1.07	161.29 ± 79.37	37.82 ± 18.70
	2	7.85	28.3	31.7	15.57	8.70 ± 3.45	2.08 ± 0.81	204.41 ± 98.75	42.31 ± 20.56
	3	6.88	27.8	30.5	15.30	17.07 ± 6.03	3.69 ± 1.29	194.97 ± 88.18	44.23 ± 20.14
	4	7.47	26.8	30.9	14.77	13.10 ± 5.12	2.81 ± 1.09	181.45 ± 92.27	38.46 ± 19.61
	5	7.32	21.1	31.4	11.61	11.32 ± 3.70	2.53 ± 0.82	101.57 ± 34.50	23.08 ± 7.71
	6	6.72	1.6	31.2	0.88	6.01 ± 2.20	2.24 ± 0.82	98.12 ± 42.06	22.44 ± 9.63
Aug. 2007	1	7.63	29.5	30.9	16.23	7.61 ± 3.15	1.73 ± 0.60	269.61 ± 126.19	59.72 ± 27.68
	2	7.93	29.1	33.7	16.01	7.60 ± 2.99	1.82 ± 0.59	179.03 ± 84.17	40.67 ± 18.91
	3	7.90	28.1	30.1	15.46	9.16 ± 3.4	2.01 ± 0.64	192.87 ± 79.45	49.14 ± 19.95
	4	7.54	28.3	31.7	15.57	7.81 ± 3.28	1.61 ± 0.59	243.18 ± 110.42	56.53 ± 25.36
	5	7.80	17.1	34.1	9.41	8.75 ± 3.22	1.75 ± 0.57	24.86 ± 9.55	7.55 ± 2.86
	6	7.76	5.0	29.5	2.75	7.60 ± 3.21	1.71 ± 0.61	17.73 ± 6.33	5.62 ± 1.99
Nov. 2007	1	8.19	28.3	31.4	15.57	7.22 ± 2.90	1.72 ± 0.64	226.22 ± 85.57	64.06 ± 23.53
	2	8.36	28.9	30.2	15.90	6.67 ± 2.68	1.42 ± 0.58	167.26 ± 67.34	47.31 ± 18.46
	3	8.10	27.9	35.5	15.35	8.30 ± 3.43	1.72 ± 0.67	275.51 ± 100.56	74.98 ± 26.59
	4	8.20	26.7	31.0	14.69	8.24 ± 3.23	1.78 ± 0.65	327.11 ± 119.74	84.53 ± 29.99
	5	8.90	15.5	31.8	8.53	8.77 ± 3.60	1.41 ± 0.56	228.60 ± 74.26	58.88 ± 18.63
	6	8.29	5.2	33.6	2.86	8.31 ± 3.49	1.55 ± 0.62	214.72 ± 82.45	59.53 ± 22.19
Feb. 2008	1	7.68	30.6	31.2	16.84	9.20 ± 3.91	2.10 ± 0.76	461.79 ± 188.87	111.04 ± 45.24
	2	7.92	31.1	31.0	17.11	8.45 ± 3.3	1.65 ± 0.63	485.14 ± 203.02	116.18 ± 48.45
	3	8.01	29.0	33.3	15.96	6.49 ±2.25	1.51 ± 0.52	404.36 ± 162.65	97.22 ± 38.95
	4	7.54	29.8	30.9	16.40	6.63 ± 2.32	1.56 ± 0.54	879.66 ± 365.74	241.76 ± 100.23
	5	8.14	27.6	31.3	15.19	7.61 ± 2.94	1.68 ± 0.62	325.79 ± 132.11	84.44 ± 34.11
	6	7.97	8.1	31.0	4.46	8.25 ± 3.47	1.58 ± 0.67	448.04 ± 173.62	111.47 ± 43.02

[*] The data referred salinity value, calculated from Pilson (1998)

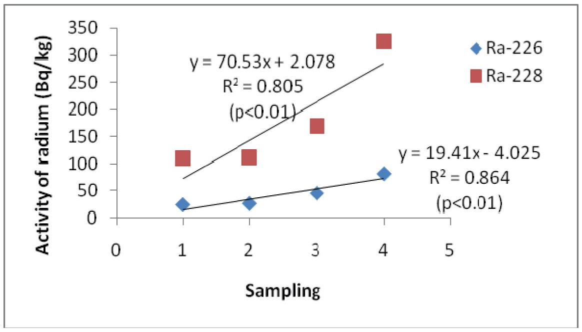


Figure 4. Relationship between radium isotopes and sampling occasions in total suspended solids (TSS_{sw}) phase in seawater (mean values of four times sampling)

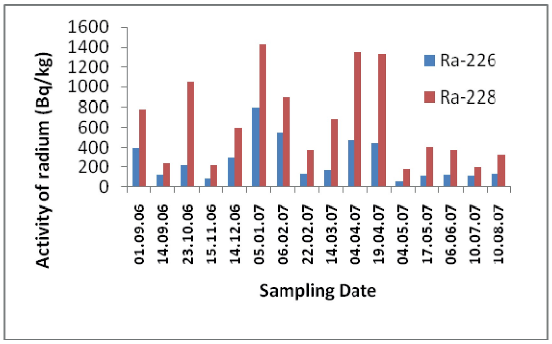


Figure 5. Collection data of mean concentration activity of radium isotopes (Bq/kg) in rainwater at Kapar Power Plant

associated to particulate matter. Furthermore, the increase of particle in radium observed in station 2 and station 4 were input of solid radioactive materials and process loading coal activities from the Kapar Power Plant.

As noted that, station 4 in February 2008, the ^{228}Ra/^{226}Ra ratio activity concentrations in total suspended solids phase (TSS_{sw}) transported by the seawater were value at 3.63, whereas in the surface sediment at this station the ^{228}Ra/^{226}Ra ratio showed opposite value at 3.49. Suspended solids were carried out by the seawater are likely to reflect mainly current discharges from power plant and industries area nearby.

3.2. Distribution of ^{228}Ra and ^{226}Ra in dissolved and total suspended solids in rainwater

The results of ^{228}Ra and ^{226}Ra at Kapar power plant are obtained during one year duration sampling from September 2006 to August 2007 and ordered according to sampling date (Table 4). Meanwhile, mean of rainfall in this one year duration period was 2.29 mm/day. The concentration of ^{228}Ra in dissolved and total suspended solid (TSS_{rw}) in rainwater gives a higher result compared to ^{226}Ra. During this sampling, a clear fluctuation of rainfall events was obtained in seasonal changes between wet season and dry season.

In this study, dry season, dusts loading for ^{226}Ra activities have been higher (803) than wet season (475) but in certain case it also can be contrast value. It is because of the early wet season after a long period of dry season will washout by the raindrops. Meanwhile for wet season, dust loading was considerably low because of lower dust suspension into the air due to wet surfaces and significant changes in radium isotopes activity throughout time and the influence of rainfall event (Table 4). With this type of climate changes, it is hard to differentiate between wet and dry seasons. Because, of the differences between wet and dry season leads to a contrast in air quality parameters mainly by content of dust loadings. This due to a combination factors, including higher wet deposition rates in the water season, lower dust suspension when the ground is wet and biomass burning, which takes place predominantly during dry season and early season (Maenhaut *et al.*, 2000).

Concentrations of ^{228}Ra and ^{226}Ra in dissolved sample at Kapar power plant are shown in Table 6.

Table 3. The activity of ^{226}Ra and ^{228}Ra at various location

Location	^{226}Ra (mBq/L)	^{228}Ra (mBq/L)	Reference
Kapar, Malaysia	1.41-3.69	6.01-17.07	This study
Nuecas Bay	2.3-16.67	2.5-43.3	Breier & Edmonds(2007)
Yeoja Bay	1.5-4.8	n.d	Hwang *et al.* (2005)
Ulsan Bay	1.4-5.4	4.49-19.9	Lee *et al.* (2005)
Estuary Nakdong	0.51-4.3	1.2-16.2	Yang *et al.* (2002)
Chao Phraya River	2.1-4.3	2.4-18.4	Nozaki *et al.* (2001)
Bengal Bay	5.4-19.0	3.0-7.6	Ghose *et al.* (2000)
South China Sea	1.30	2.98	Nozaki & Yamamoto (2001)
Mississippi & Atchafalaya	1.2-3.3	0.7-7.4	Krest & Moore (1997)
Bengal Bay	2.0-19.0	0.3-44.2	Moore (1997)

Table 4. Activity concentration of ^{228}Ra and ^{226}Ra in dissolved and total suspended solids (TSS$_{rw}$) in rainwater

Sampling Date	**pH**	**Rainfall (mm/day)**	**^{226}Ra**		**^{228}Ra**		**^{228}Ra/^{226}Ra**	
			RW (mBq/l)	**TSS$_{rw}$ (Bq/kg)**	**RW (mBq/l)**	**TSS$_{rw}$ (Bq/kg)**	**RW**	**TSS**
			(*n=6*)	**(*n=6*)**	**(*n=6*)**	**(*n=6*)**		
1-Sep-06	4.75	1.56	124.25 ± 8.18	414.21 ± 106.99	378.18 ± 76.91	675.08 ± 271.09	3.04	1.63
14-Sep-06	5.40	2.20	25.96 ± 9.30	103.61 ± 31.34	79.77 ± 41.39	369.56 ± 162.82	3.07	3.57
4-Oct-06	-	-	-	-	-	-	-	-
23-Oct-06	5.43	1.99	2.73 ± 1.56	219.18 ± 71.19	10.97 ± 4.68	641.91 ± 237.81	4.01	2.93
15-Nov-06	6.32	2.15	7.84 ± 2.23	91.03 ± 4.32	29.76 ± 13.08	339.11 ± 100.34	3.79	3.73
4-Dec-06	-	-	-	-	-	-		
14-Dec-06	5.71	1.69	7.91 ± 3.59	294.63 ± 2.88	23.35 ± 10.01	378.25 ± 117.22	2.95	1.28
5-Jan-07	6.11	13.35	7.09 ± 2.00	167.24± 32.74	17.74 ± 7.38	439.17 ± 152.65	2.50	2.63
21-Jan-07	-	-	-	-	-	-	-	-
6-Feb-07	5.38	1.30	25.92 ± 5.67	552.11 ± 109.53	112.13 ± 34.09	675.81 ± 256.65	4.33	1.22
22-Feb-07	5.72	0.79	17.47 ± 5.58	136.95 ± 4.93	78.58 ± 34.44	483.65 ± 148.45	4.50	3.53
14-Mar-07	5.33	3.89	2.00 ± 0.61	177.99 ± 32.95	8.38 ± 3.65	418.09 ± 137.82	4.18	2.35
4-Apr-07	6.19	0.79	8.19 ± 2.51	475.32 ± 143.77	34.12 ± 14.88	876.59 ± 363.28	4.17	1.84
19-Apr-07	5.34	3.07	5.10 ± 1.58	448.18 ± 146.74	22.47 ± 9.62	633.06 ± 278.62	4.40	1.41
4-May-07	4.66	3.28	11.58 ± 3.65	60.68 ± 20.91	53.34 ± 22.80	291.21 ± 140.63	4.61	4.80
17-May-07	5.79	1.06	28.83 ± 9.43	115.17 ± 37.61	136.77 ± 59.91	463.47 ± 201.31	4.74	4.02
6-Jun-07	5.15	2.31	30.81 ± 9.64	127.83 ± 56.33	121.45 ± 34.85	439.52 ± 128.69	3.94	3.44
22-Jun-07	-	-	-	-	-	-	-	-
10-Jul-07	5.78	2.67	15.77 ± 4.87	116.08 ± 34.61	68.02 ± 29.01	406.24 ± 166.78	4.31	3.50
27-Jul-07	-	-	-	-	-	-	-	-
10-Aug-07	5.15	4.05	5.77 ± 1.66	131.58 ± 4.31	22.12 ± 9.30	372.09 ± 114.52	3.84	2.83

*The RW is dissolved phase and TSS$_{rw}$ is total suspended particulate phase in rainwater

*The (-) is don’t have rain during sampling period

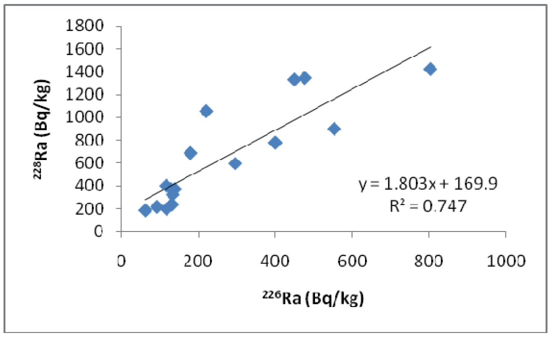


Figure 6. Correlation between ^{226}Ra and ^{228}Ra in total suspended solids (TSS_{rw}) phase in rainwater

Relatively high concentration of dissolved ^{228}Ra in rainwater in first sampling is due to weathering of early wet season (Table 4). These results were fluctuation during this sampling study. When the seasonal monsoon was exchange, it will give the different results which are probably higher concentration activity of radium isotopes. Radium isotopes activities in dissolved phase of rainwater obtained from Kapar power plant were varied from 2.67 to 124.25 mBq/L for ^{226}Ra and 6.41 to 242.31 mBq/L for ^{228}Ra. Then the ^{226}Ra and ^{228}Ra in total suspended solids (TSS_{rw}) of rainwater were range from 60.68 to 803 Bq/kg and 187–1423 Bq/kg, respectively (Table 4 and Fig. 5).

In total suspended solids (TSS_{rw}) phase was varied depend on rainfall event and it was proven by an ANOVA analysis that have significant difference 95% confidence for activities of ^{228}Ra ($p=0.013$) and ^{226}Ra ($p=0.001$). The statistical correlation between radium activity and rainfall event at coal electric burning found that medium positive correlated with Pearson correlation, $r = 0.548$ for ^{226}Ra and probably due to low dilution occurred in different source at Kapar power plant.

The activity ratios of ^{228}Ra/^{226}Ra in dissolved and particulate phases of rainwater obtained from Kapar power plant were varied in the range of 1.82 to 3.04 and from 1.63 to 3.87 respectively, where the ^{228}Ra are more abundance in the dissolved phase and opposite shown by ^{226}Ra. Contrast in suspended particle matter phase, shown that relationship between ^{228}Ra and ^{226}Ra are strong Pearson correlated, $r = 0.864$ (Fig. 6). This might suggested a large portion of input isotope ^{228}Ra was occurred into the rainwater water at Kapar power plant.

3.3. Variations of pH in Rainwater

Fig. 7(i) shows the temporal variation of pH in rainwater at Kapar coal burning area during September 2006 to August 2007. During this study, the pH of rainwater ranged from pH 4.66 to pH 6.32, with an average pH 5.51, for Kapar coal burning area was still within the range of unpolluted rainwater, pH 5.6 being the limiting pH value of clean rainwater, which is slightly acidic as a result of dissolution of CO_2 in water. This average value was also well above pH 4.3 as the mean pH for urban Petaling Jaya (Siti Mariam *et al.*, 2005), Sabah at pH 5.17 in Danum Valley (Siti Mariam *et al.*, 2009) or areas subjected to acidic precipitation as pH 4.7 in North eastern China (Wang *et al.*, 2008). The frequency distribution of pH as shown in Fig. 7(ii) shows about 12.5% of the total rainfall in Kapar coal burning area can be considered acidic (<pH 5.0), whereas 43.8% of rainwater accounted for mildly acidic (pH 5.0 – pH 5.6). Only 25% of the precipitation recorded can be categorized as slightly alkaline (pH 5.6 – pH 6.0). Samples with very alkaline (>pH 7.0) was not observed, indicating the absence of strong influence of basic species. These results demonstrated that strong influence of neither strong acids nor alkaline components was impacting Kapar coal burning area resulting in volume weighted mean pH of 5.51, slightly

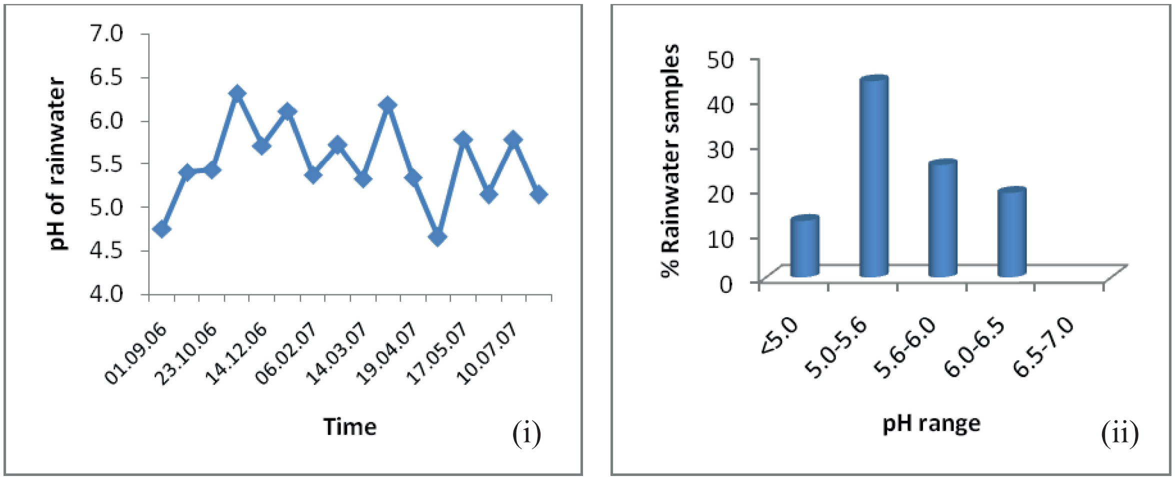
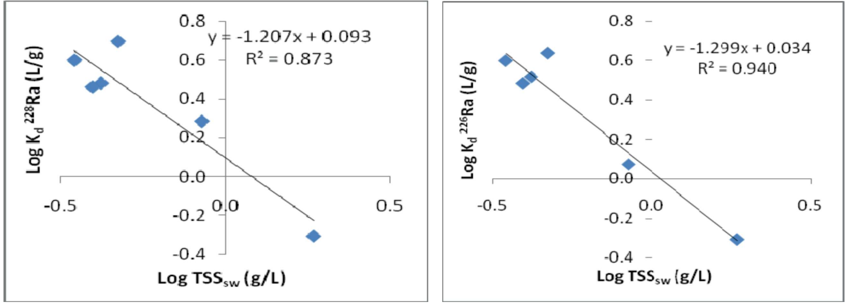
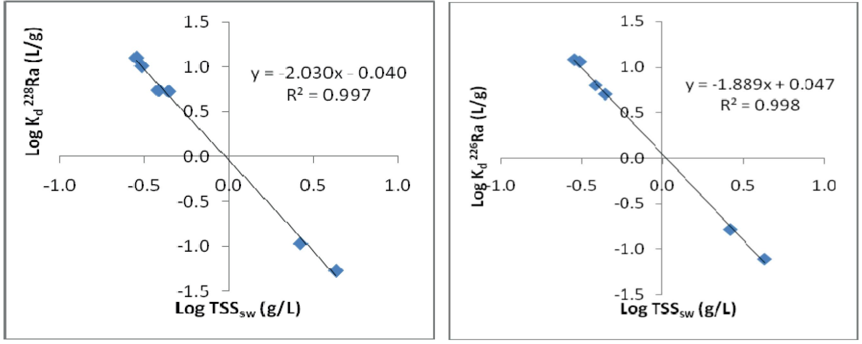


Figure 7. (i) Temporal variation of pH; (ii) percent pH distribution for rainwater

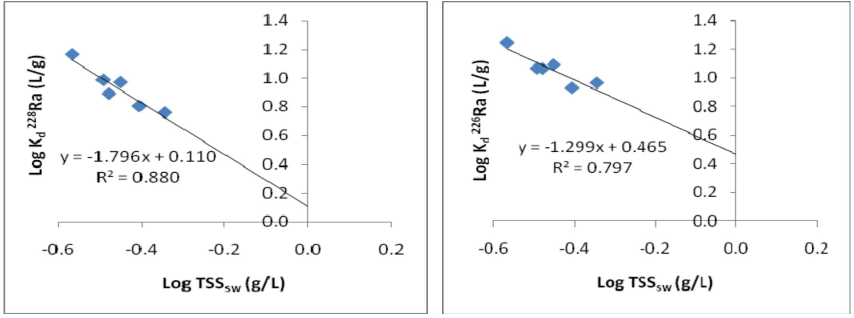
i) March 2007



ii) August 2007



iii) November 2007



iv) February 2008

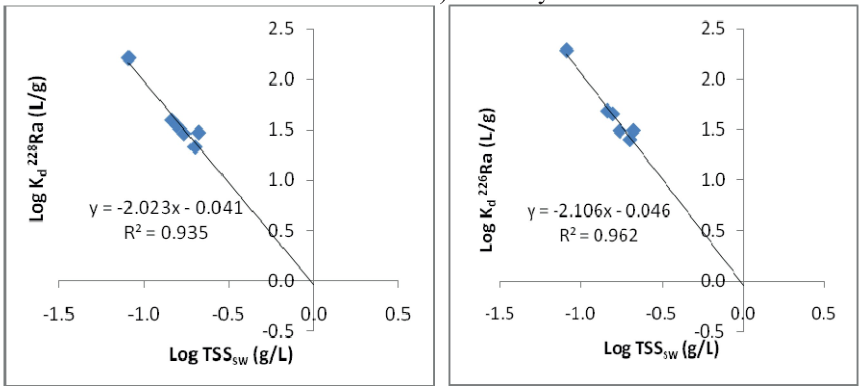


Figure 8. Correlation between log K_d with log TSS$_{sw}$ for ^{228}Ra and ^{226}Ra at six stations at Kapar coastal area obtained on i) March 2007 ii) August 2007 iii) November 2007 and iv) February 2008

Table 5. Distribution coefficient in seawater obtained during this study at Kapar coastal water

Stn.	**TSS_{sw} (g/L)**				**K_d $^{228}Ra \times 10^4$ (L/g)**				**K_d $^{226}Ra \times 10^4$ (L/g)**				**K_d ^{228}Ra/ K_d ^{226}Ra**			
	Mar 07	Aug 07	Nov 07	Feb 08	Mar 07	Aug 07	Nov 07	Feb 08	Mar 07	Aug 07	Nov 07	Feb 08	Mar 07	Aug 07	Nov 07	Feb 08
1	0.4175	0.2845	0.3220	0.1723	3.039	12.458	9.724	29.128	3.289	12.123	11.599	30.677	0.924	1.028	0.838	0.949
2	0.4705	0.4420	0.3925	0.1451	4.995	5.332	6.385	39.577	4.317	5.059	8.478	48.402	1.157	1.054	0.753	0.818
3	0.3931	0.3841	0.3543	0.2094	2.905	5.484	9.372	29.758	3.049	6.349	12.309	30.829	0.953	0.864	0.761	0.965
4	0.3465	0.3058	0.2715	0.0810	3.996	10.181	14.622	163.897	3.953	11.518	17.532	191.536	1.011	0.884	0.834	0.856
5	1.8518	2.6383	0.4525	0.1995	0.494	0.108	5.762	21.445	0.492	0.164	9.198	25.208	1.005	0.659	0.626	0.851
6	0.8452	4.2921	0.3320	0.1557	1.932	0.054	7.787	34.883	1.183	0.077	11.545	45.295	1.634	0.710	0.674	0.770

below pH 5.6. Thus even remote areas like Kapar, which is regarded as pristine with limited human activities, impact from some acidic influence created elsewhere cannot be totally ruled out.

3.4. Distribution coefficient values, (K_d) of ^{228}Ra and ^{226}Ra

Distribution coefficients, K_d value are widely used as a first approach to the understanding and determination of the metals and radionuclides released into the aquatic environment. Based on some physical and chemical aspects of the interaction between the soluble and insoluble phases, some equations have been developed to explain some features of the observed Kd variability quantitatively (Abril and Fraga, 1996). In this study, the distribution coefficient is defined as;

$$K_d = \frac{(A)_P}{(A)_D \text{ x } TSS_{sw}}$$

Where the (A)p is the activity of particulate ^{226}Ra or ^{228}Ra (Bq/kg), (A)D is the activity of dissolved ^{226}Ra or ^{228}Ra (Bq/L) and TSS_{sw} is the amount of total suspended solids in seawater (g/L). The calculated K_d values of ^{228}Ra and ^{226}Ra are ranged from 0.054 × 104 to 163.90 × 104 L/g and between 0.49 × 104 to 191.54 × 104 L/g, respectively (Table 5).

The K_d value of ^{228}Ra and ^{226}Ra is plotted against the particle concentration on March 2007, August 2007, November 2007 and February 2008 (Figure 8). Negative log K_d versus TSM correlation has been observes for ^{228}Ra and ^{226}Ra in this study. Several hypotheses have been proposed for this observation but it appears that coagulation of colloidal size particles most likely play an important role (Wei and Murant, 1994).

A negative statistical correlation ($r^2>0.79$) during dry and wet seasons has been showed from the plotted ^{228}Ra and ^{226}Ra values against the amounts of particle concentration. The distribution coefficients ratio (Kd ^{228}Ra/Kd ^{226}Ra) also calculating during both season was varied from 0.659 to 1.634 and 0.626 to 0.965 for dry season (March and August) and wet season (November and February), respectively. The activity ratio (AR) >1.0 means that high strongly suggest that the preferential adoption of ^{228}Ra was much relative than ^{226}Ra by the particulate materials.

4. Conclusion

Total suspended solids give the highest values of radium compared with dissolve phase of seawater and rainwater samples. Rainwater samples in Kapar coal-fired power plant gives a fluctuated result of radium activity during the study because the contribution from the fly ash of coal burning operation.

Acknowledgement

The authors would like to thank all individuals and organizations involved in this research, particularly the Universiti Kebangsaan Malaysia and Kapar Energy Ventures Sdn. Bhd. for their invaluable help. This research is funded by the Ministry of Science, Technology and Innovation, Malaysia (Science Fund grant No. 04-01-02-SF0117).

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Received 29 May 2010
Accepted 17 June 2010

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