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Rare Earth Elements in the Water Column of Sungai Balok, Pahang, Malaysia as Monsoon Event Proxies

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Abstract

Sampling of surface water at seven stations along the Sungai Balok, Pahang was conducted from 2013 to 2015 to investigate the distribution of dissolved rare earth elements (REE) in river systems. The whole concentration of ΣREE in the dissolved phase recorded during this study ranged from 368 to 9121 pmol·L^{-1} with a mean of 2328 ± 1442 pmol·L^{-1} that was dominantly influenced by the concentration of Ce ranging from 84 to 3237 pmol·L^{-1}. Similarly, the large ranged value of La/Yb$_N$ (0.69 - 11.57) might be due to the fluctuating rainfall events during samplings as well as input from lithogenic sources that suggests the influence of monsoon events. The highly significant statistical correlation of Al and Fe (R^2 = 0.65; $p < 0.01$) also suggests the resuspension and mixing of REEs in the water column. However, the lower ratio of Y/Ho < 55 might be due to the large volume of freshwater input especially during the Northeast monsoon (November to March). Therefore, the highest inventories of Ce were during 15th January 2014 and 1st November 2014 with 586.5 pmol·cm^{-2} and 643.4 pmol·cm^{-2}, accordingly. Subsequently, results showed an increasing flux of Ce occurring in the dissolved phase from November 2013 to January 2014 and November 2014 to January 2015, with 39.14 nmol·cm^{-2}·yr^{-1} and 59.78 nmol·cm^{-2}·yr^{-1}, respectively.

Keywords

Rainfall, Sediment, Water Column, Monsoon, Dissolved Phase

1. Introduction

Studies on distributions of dissolved REEs in river and marine environments were previously conducted based on river discharge loadings, rainfall and sources of geology such as granite and carbonatite [1]. The distribution of dissolved REEs in the marine environment is attributed to the affinity of water to dissolved minerals onto the particle surface [2]. Therefore, dissolved REEs in river systems are associated with monsoon events that were explained previously e.g. river discharge, geological input and rainfall distribution in the Chow Phraya River, Thailand and Mandovi River, India [3]. The abundance of REEs in the dissolved phase of tropical rivers usually corresponds to salinity, carbonate complex and biological processes [4].

The monsoon period of the southern South China Sea is always changing and not fixed every year. Therefore, this study is important to examine the presence of monsoon effects over sampling periods with the climatological data of wind flow direction and rainfall distribution. The distribution of REEs in dissolved phases had been observed in various environments such as global rivers [5], biogeochemical cycles in Tokyo Bay [6], granite sources [7], and most recently published in the Bay of Bengal by Yu *et al.* (2017) [8]. Dissolved REEs in rainwater have been discussed based more on industrial effects e.g., mining and atmospheric pollutants during wet deposition within acidic rainwater [9]. However, the rainfall aspect in tropical river systems and changing monsoons have not been well discussed by the previous researchers and in this study the authors have selected the Sungai Balok, Pahang, Malaysia as a pilot study area to elucidate REEs with rainfall events.

The upstream of Sungai Balok is in the hilly mountain near the granite belt [10] therefore, the river receives large amounts of dissolved and particulate loads due to heavy rainfall events especially during the Northeast monsoon. The increase in river discharge also brings higher terrestrial inputs as well as erodes the mangrove forest in the river system. The idea of establishing selected REE proxies *i.e.*, La/Yb and Y/Ho was conducted previously in studies on dissolved REE in rainwater but overlooked the abundance of La compared Ce and the positive anomaly of Ce and Gd. This however, was not used to directly determine any REE proxies for studying the monsoon changes. Since La/Yb_N was used by Thompson *et al.* (2013) [11], and Takahashi and Noriki (2007) [6] in the estuaries of several major rivers around the world and in Tokyo Bay, respectively, it was deduced to have the potential to be the REE proxy in Sungai Balok for the determination of the monsoon due to rainfall seasonality [12]. The terrigenous detritus also contains lithogenic sources including organic and inorganic components through the weathering in estuarine environments. Meanwhile, previous studies on higher dissolved REE concentrations from lithogenic organic sources were investigated in Tokyo Bay [6] as well as Bay of Bengal [13]. Hence, the objective of this study is to investigate the distribution of REEs during various sampling periods and to determine the suitable proxy of lithogenic sources using a species of REEs.

2. Sampling and Analytical Procedures

Sungai Balok is located on the East coast Peninsular of Malaysia with water depths ranging from 0.5 - 6 m, length is ~5 km and the average width is ~13.3 m. The estuarine and river systems are surrounded by mangrove forests and undergo semi-diurnal tides. Surface water was collected using a clean water sampler at seven stations of the river during nine sampling trips from 2013 to 2015 (**Table 1**; **Figure 1**). In the laboratory, water samples were filtered immediately using 0.45 μm membrane filter paper and acidified to pH 2. The filtrate was in the dissolved form while the samples remaining on the filter paper were considered suspended particles samples. Dissolved samples were then stored in acid washed polyethylene bottle [7] with 50 ml of 4% HNO_3 and kept in a cool box prior to further analysis in the laboratory. Water quality parameter *i.e.*, salinity, was also recorded using the calibrated water quality multi-parameter AAQ-1183H manufactured by Alec Electronics Co. Ltd.

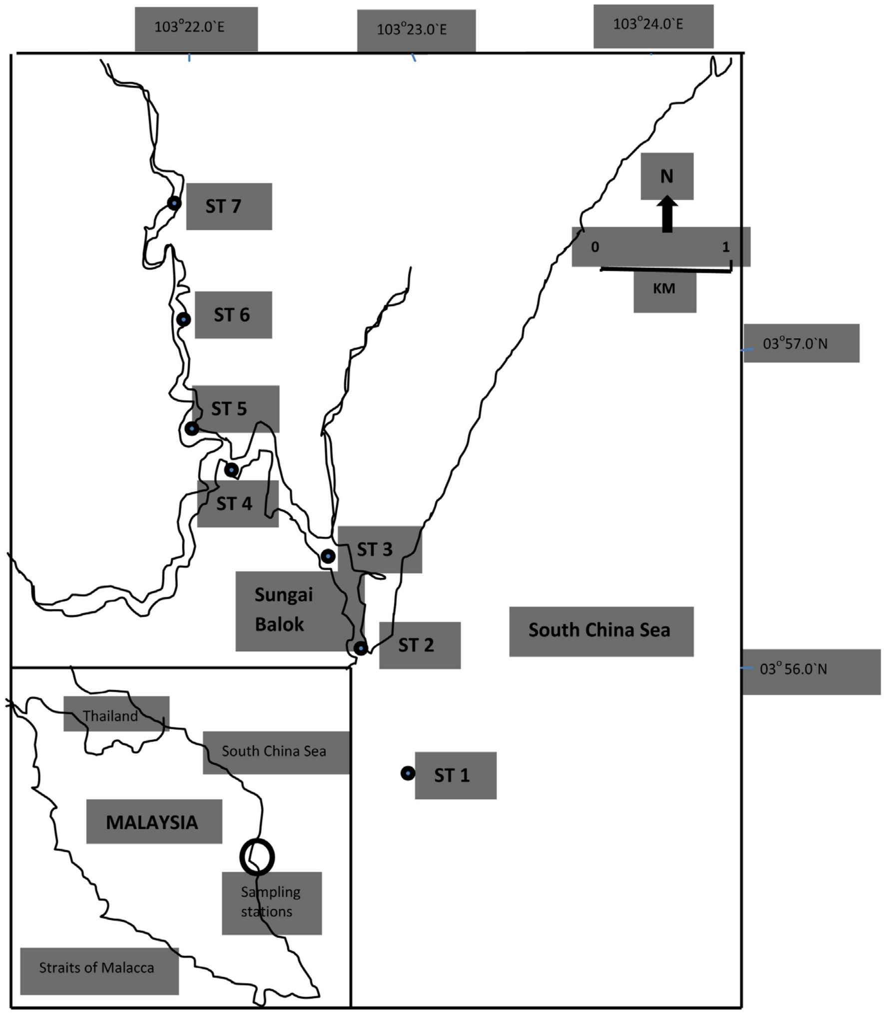


Figure 1. The map of location sampling of Sungai Balok also including the respectively depth with ST1 (6 m); ST2 (0.5 m); ST3 (1.5 m); ST4 (4 m); ST5 (5 m); ST6 (5 m) and ST7 (4.8 m). Sampling station also divided into three categories as coastal zone (ST1 and ST2), estuarine zone (ST3, ST4 and ST5) and river zone (ST6 and ST7). About nine times of sampling were conducted as 16-Jan-2013, 24-April-2013, 16-July-2013, 01-November-2013, 15-January-2014, 24-April-2014, 17-July-2014, 01-November-2014 and 31-January-2015.

Table 1. GPS coordinates of sampling stations at the Sungai Balok.

Area	Station (ST)	GPS coordinates		Depth (m)	Remarks
		Latitude (N)	Longitude (E)		
Coastal	1	03˚55.714'	103˚22.884'	6	Extension from river mouth
	2	03˚55.928'	103˚22.652'	0.5	Sand bar area
Estuarine	3	03˚56.242'	103˚22.443'	1.5	Junction to Sungai Tungkak
	4	03˚56.630'	103˚22.086'	4	Junction to Sungai Pengkalan Baru
	5	03˚56.780'	103˚21.974'	5	Mangrove and nymph forest
River	6	03˚57.140'	103˚21.800'	5	Mangrove and nymph forest
	7	03˚57.410'	103˚21.720'	4.8	Mangrove and nymph forest

The published analytical procedure was followed with the pre-concentration method using Chelex-100 resin [14]. While the trace elements such as Al, Mn and Fe were also analyzed using the published protocol of Bourg (1983) [15]. The Standard Reference Material (SRM) was also prepared by spiking multi-REE elements (10 ppm) and standard solution of trace elements (10 ppm) into artificial seawater and running them as actual samples to observe their recovery yield (90% - 95%). The concentration levels of biological silicate (Biogenic SiO_2) were determined using the yellow silicomolybdate techniques Coradin *et al.*, (2004) [16].

The results of REEs have been normalized with the Post Archean Australian Average Sedimentary rock or Shale (PAAS), which is the nearest continental crust for further discussion [7]. According to Daud and Mohamed (2016) [1], the geological setting of Sungai Balok is enriched with sedimentary rock or clay along basaltic rock, which is similar to PAAS. Generally the REEs members will divide into two groups as light rare earth element (LREE) which in the periodic table is from lanthanum (La) to Europium (Eu) and heavy rare earth element (HREE) is from gadolinium (Gd) to lutetium (Lu). Subsequently, the estimated flux of REE in Sungai Balok was calculated using the following published Equation (1) [17].

$$\text{Flux} = \text{The sampling period}\left(\text{day}\cdot\text{yr}^{-1}\right)\times 86400\ \text{s}\cdot\text{day}^{-1}\frac{1}{N}\sum_{i=1}^{N}c\left(ti\right)\times Q\left(ti\right) \quad (1)$$

The ratio of $\frac{1}{N}$ is a conversion factor which is obtained from days of sampling period per year while 86,400 is the calculated seconds per day value. The $c(ti)$ is concentration of represented dissolved REE ($pmol\cdot L^{-1}$) and $Q(ti)$ is the average daily river discharge in $L\cdot s^{-1}\cdot km^{-2}$ or $m^3\cdot s^{-1}\cdot km^{-2}$. According to DID (2011) [18], the National water resources report has stated that Sungai Balok has similar category of a small tributary such as Sungai Lepar near the major river of Sungai Pahang with daily discharge of ~4.59 $m^3\cdot s^{-1}$ or 4.59 × 10^3 $L\cdot s^{-1}$ while the size of the river area is ~66.5 × 10^{-3} km^2. The statistical analysis used was the correlation matrix and ANOVA using SPSS version 21 to determine a significant correlation and differences of selected total dissolved REE concentrations, the REE proxy ratios and some essential elements where statistically significant and different when $p \leq 0.05$ or 0.01.

3. Results and Discussions

3.1. Rare Earth Element in Dissolved Phase

The distribution of dissolved REEs varies from upstream to downstream especially during November and January. During this period, the total dissolved rare earth elements (ΣREEs) ranged from 368 to 9121 pmol·L^{-1}, with a mean value of 2328 ± 1442 pmol·L^{-1}, and LREE/HREE ratio ranging from 5.20 ± 0.97 to 22.41 ± 3.00 (**Table 2**). The LREE concentrations along the sampling stations ranged from 344 to 8724 pmol·L^{-1} and HREE from 23.5 to 593 pmol·L^{-1}. According to McLennan (1989) [19] the abundance of total dissolved REEs strongly supports the huge concentration of Cerium (Ce). The concentrations of Ce also varied between 84 to 3237 pmol·L^{-1} with the highest mean concentration of 1680 ± 730 pmol·L^{-1} recorded in November 2014 (**Table 2**). These results were probably due to the high rainfall events [14]. Dissolution of Ce in January 2014 was observed to be statistically higher due to the higher monthly rainfall distribution ($r = 0.328$; $p < 0.05$) with 277 mm (**Figure 2**). The same results were obtained after the flooding disaster in December 2013 due to heavy rainfall (>1800 mm) as well as in November 2014 when the rainfall was about 288 mm. Hence these incidents have increased the REE contents in the water column.

There were no significant differences and distributions of REE contents among the stations from upstream to downstream ($p > 0.05$) except between sampling periods ($p < 0.05$) because the depth of the water column is very shallow e.g., less than 5 m during high tide which might have caused active resuspension. According to Shynu *et al.* (2011) [3] the resuspension activities of dissolved REEs in rivers might be from surface sediment to water column as well as re-suspended in subsurface waters from the river runoff. The resuspension and mixing process of REEs in the water column was also observed based on the significant statistical correlation between Al and Fe ($R^2 = 0.65$; $p < 0.01$) that was discussed previously in Bourg (1983) [15]. Regarding the concentration of Fe and Al that showed opposite trends to concentration of dissolved REEs, the species in **Table 2** might be desorbed from particles or resuspended from surface sediment. This may have been caused by active river discharge transportation from the upper stream after incorporation of heavy rainfall and sources from groundwater discharge [12].

The sampling sites were divided into three zones which were river, estuarine and coastal (**Table 1**; **Figures 3(b)-(d)**) to examine the dissolved REE concentrations based on the salinity gradient whereby 27 - 33 psu, 13 - <27 psu and <13 psu represent coastal, estuary and river areas, respectively. The concentrations of ΣREEs slightly decreases towards the estuarine zone (mean range: 514 - 3713 pmol·L^{-1}) and increases in the coastal zone (mean range: 387 to 6087 pmol·L^{-1}).

Table 2. Concentrations of selected dissolved REE (pmol·L^{-1}) of Y, Ce, Nd, Eu and Ho, LREE, HREE and Total REE, the ratios of Ce/Ce*, Eu/Eu*, Y/Ho, La/Yb$_N$, and selected essential elements (μmol·L^{-1}) of Fe, Mn and Al in Sungai Balok.

Date/ period	Station	Salinity	Y	Ce	Nd	Eu	Ho	L/HREE	LREE	HREE	ΣREE	La/Yb$_N$	Ce/Ce*	Eu/Eu*	Y/Ho	Fe	Mn	Al
	ST1	30.16	342	323	147	4.340	2.480	4.750	798	168	966	0.897	0.690	0.377	138	16.61	0.115	7.760
	ST2	14.02	311	317	154	6.263	1.640	6.580	731	111	842	1.550	0.870	0.601	190	13.09	0.123	7.950
	Mean	22.09	327	320	150	5.302	2.060	5.665	765	140	904	1.224	0.780	0.489	164	14.85	0.119	7.855
16 Jan 13	ST3	7.400	246	401	148	19.61	1.667	4.390	816	186	1002	0.920	1.150	1.170	147	16.68	0.303	8.090
	ST4	2.710	350	561	344	15.32	5.240	4.430	1436	325	1761	0.690	0.720	0.597	66.80	13.64	0.356	5.790
	ST5	0.660	306	562	230	26.71	3.000	5.840	1229	211	1440	1.160	1.000	1.210	102	13.64	0.507	5.800
	Mean	3.590	301	508	241	20.55	3.302	4.887	1160	241	1401	0.923	0.957	0.992	105	14.65	0.389	6.560
	ΣMean	10.99	311	433	205	14.45	2.805	5.198	1002	200	1202	1.043	0.886	0.791	129	14.73	0.280	7.078
	s.d	11.88	41.00	122	85.41	9.310	1.480	0.970	312	78.88	385	0.330	0.190	0.330	46.70	1.760	0.165	1.180
	ST1	31.66	77.47	132	68.38	1.766	1.148	14.66	344	23.50	368	3.200	0.600	0.892	67.48	14.07	0.020	4.770
	ST2	31.56	85.50	164	71.58	1.500	1.439	12.61	376	29.80	406	1.980	0.757	0.710	59.42	13.84	0.016	8.660
	Mean	31.61	81.49	148	69.98	1.633	1.294	13.64	360	26.65	387	2.590	0.679	0.801	63.45	13.96	0.018	6.715
24 April 13	ST3	31.44	76.00	184	73.83	1.816	1.088	14.95	389	26.01	415	2.300	1.190	0.802	69.85	15.43	0.018	4.870
	ST4	20.93	45.46	179	71.80	1.684	0.900	18.32	403	22.15	425	3.100	0.967	0.835	50.51	11.00	0.575	4.660
	ST5	18.82	96.37	372	78.10	3.090	1.560	13.80	655	47.50	703	1.590	1.270	0.873	61.77	12.48	0.890	8.810
	Mean	23.73	72.61	245	74.58	2.197	1.183	15.69	482	31.89	514	2.330	1.142	0.836	60.71	12.71	0.494	6.113
	ST6	8.940	103	499	114	3.030	1.730	17.61	892	50.00	942	2.580	1.240	0.680	59.50	16.13	1.205	4.780
	ST7	2.460	224	604	139	6.080	2.450	13.53	1174	86.79	1261	1.730	0.880	0.830	91.42	16.43	1.066	11.89
	Mean	5.700	164	552	127	4.555	2.090	15.57	1033	68.40	1102	2.155	1.060	0.755	75.46	16.28	1.136	8.335
	ΣMean	20.83	101	305	88.10	2.710	1.474	15.07	605	40.82	646	2.354	0.986	0.803	65.71	14.19	0.541	6.920
	s.d	11.75	57.24	188	27.36	1.620	0.520	2.130	321	23.21	343	0.640	0.258	0.080	12.95	1.980	0.526	2.880
	ST1	32.41	201	325	140	16.84	3.880	13.91	1146	82.00	1228	3.58	0.340	2.600	51.80	17.54	0.067	5.180
	ST2	31.97	176	274	125	5.530	2.790	15.61	1041	66.70	1108	3.72	0.300	1.080	63.08	21.41	0.073	4.860
	Mean	32.19	189	290	133	11.19	3.335	14.76	1094	74.35	1168	3.65	0.320	1.840	57.44	19.48	0.070	5.020
16 July 13	ST3	32.29	263	244	125	15.26	16.85	6.68	977	146	1123	1.880	0.290	2.230	3.750	20.07	0.135	7.650
	ST4	15.25	464	281	210	13.29	9.940	23.10	3855	167	4022	10.34	0.060	1.150	46.68	15.98	2.562	14.72
	ST5	9.060	569	352	327	12.37	7.760	10.45	2045	196	2241	3.960	0.200	0.730	73.32	22.14	2.437	26.36
	Mean	18.87	432	292	221	13.64	11.52	13.41	2292	170	2462	5.393	0.183	1.370	41.25	19.40	1.711	16.24
	ST6	2.240	811	1430	538	33.82	15.64	12.11	3876	320	4196	4.110	0.560	1.290	64.64	29.14	2.000	21.66
	ST7	0.240	410	938	275	36.32	4.120	17.49	2359	135	2494	5.430	0.617	2.330	99.50	24.20	0.990	13.65
	Mean	1.240	611	1184	407	35.07	9.880	14.80	3118	228	3345	4.770	0.589	1.810	82.07	26.67	1.495	17.66
	ΣMean	17.64	413	549	249	19.06	8.711	14.19	2186	159	2344	4.717	0.338	1.630	57.54	21.49	1.181	13.44
	s.d	14.45	226	457	149	11.52	5.720	5.280	1261	84.18	1326	2.690	0.195	0.736	29.25	4.360	1.130	8.280
	ST1	31.84	169	307	119	30.24	25.64	7.660	1867	244	2111	3.085	0.164	2.520	6.590	4.790	1.685	14.72
	ST2	31.75	27.25	84.00	35.14	10.03	7.550	5.550	371	66.50	438	1.470	0.258	4.080	3.610	4.460	1.058	18.07
	Mean	31.80	98.13	196	77.07	20.14	16.60	6.605	1119	155	1274	2.278	0.211	3.300	5.100	4.625	1.372	16.40
1 Nov 13	ST3	31.64	64.56	181	59.17	9.630	6.580	7.330	490	66.5	557	1.460	0.547	2.980	9.810	10.07	1.284	27.98
	ST4	9.300	80.52	299	106	17.13	10.09	9.570	1067	111	1178	2.520	0.336	2.760	7.980	6.783	5.447	17.70
	ST5	9.000	68.26	250	85.83	9.170	5.970	12.64	813	64.20	877	3.240	0.380	2.560	11.43	13.26	4.928	12.87

Continued

	Mean	16.65	71.11	243	83.67	11.98	7.547	9.847	790	80.57	871	2.407	0.421	2.767	9.740	10.04	3.886	19.52
	ST6	4.200	51.98	198	63.61	8.840	5.850	9.320	542	57.60	599	1.970	0.521	3.030	8.880	12.66	8.361	14.83
	ST7	1.410	128	611	202	16.74	7.790	10.63	1140	107	1247	1.070	1.330	2.330	16.43	39.55	2.036	26.52
	Mean	2.805	89.99	405	133	12.79	6.82	9.975	841	82.30	923	1.520	0.926	2.680	12.66	26.11	5.199	20.68
	ΣMean	17.02	84.22	276	95.88	14.54	9.920	8.860	899	102	1001	2.116	0.505	2.894	9.247	13.08	3.543	18.96
	s.d	14.04	48.38	166	54.90	7.790	7.080	2.340	518	23.65	579	0.850	0.388	0.580	4.026	12.02	2.760	5.960
	ST1	27.60	449	1443	472	36.89	13.18	14.25	3663	257	3920	2.820	1.080	2.350	34.07	8.080	0.816	12.36
	ST2	20.73	382	1757	657	36.89	13.58	18.04	4520	250	4770	5.170	0.881	1.880	28.13	10.29	0.455	16.30
	Mean	24.17	416	1600	565	36.89	13.38	16.15	4092	254	4345	3.995	0.981	2.115	31.10	9.185	0.636	14.33
15 Jan 14	ST3	7.480	169	717	405	14.00	10.03	20.59	2682	131	2813	8.040	0.315	1.800	16.91	5.996	0.230	9.990
	ST4	2.110	347	1788	1273	52.82	11.22	22.00	5648	257	5905	9.770	0.426	1.180	18.84	10.18	1.239	11.34
	ST5	1.960	145	649	380	11.76	7.450	23.23	2322	100	2422	7.410	0.437	2.290	19.42	5.590	0.230	8.290
	Mean	3.850	220	1051	686	26.19	9.567	21.94	3551	163	3713	8.410	0.393	1.760	18.39	7.260	0.566	9.870
	ST6	1.310	378	3237	1768	67.37	20.70	22.00	8724	397	9121	5.370	0.514	1.510	18.26	9.600	0.670	3.180
	ΣMean	10.20	311	1598	826	36.62	12.69	20.02	4593	232	4825	6.430	0.609	1.835	22.60	8.289	0.607	10.24
	S.d	11.25	125	943	569	21.62	4.510	3.340	2360	106	2460	2.470	0.300	0.450	6.890	2.090	0.388	4.385
	ST1	32.48	403	1900	764	85.00	42.91	10.50	5193	495	5688	2.390	0.556	2.950	9.390	0.773	0.102	2.550
	ST2	32.40	292	1314	394	29.74	15.27	13.61	3237	238	3475	3.920	0.662	1.540	19.12	0.477	0.027	1.560
	Mean	32.44	348	1607	579	57.37	29.09	12.06	4215	367	4582	3.155	0.609	2.245	14.26	0.625	0.065	2.055
24 April 14	ST3	31.75	311	593	292	17.89	13.94	8.860	1507	170	1677	1.530	0.221	1.700	22.31	0.868	0.066	1.300
	ST4	23.68	247	580	201	15.79	11.52	10.96	1547	141	1688	2.530	0.566	1.640	21.44	0.814	0.036	2.460
	ST5	22.50	136	555	255	21.24	14.06	10.15	1436	141	1577	1.950	0.629	2.390	9.670	0.707	0.025	1.450
	Mean	25.98	231	576	249	18.31	13.17	9.990	1497	151	1647	2.003	0.472	1.910	17.81	0.796	0.042	1.740
	ST6	20.07	137	509	204	14.34	9.820	12.18	1222	100	1322	2.360	0.700	2.140	13.91	0.750	0.028	4.550
	ST7	6.820	120	607	234	16.84	9.700	13.50	1476	109	1585	2.720	0.673	1.820	12.42	0.405	0.004	2.250
	Mean	13.45	129	558	219	15.59	9.760	12.84	1349	105	1454	2.540	0.687	1.980	13.17	0.578	0.016	3.400
	ΣMean	24.24	235	865	335	28.69	16.75	11.39	2231	199	2430	2.486	0.572	2.025	15.46	0.684	0.041	2.300
	s.d	9.260	108	535	200	25.14	11.74	1.780	1472	138	1607	0.750	0.164	0.505	5.450	0.175	0.033	1.112
	ST1	32.26	153	219	163	3.680	2.060	19.09	778	40.76	818	2.960	0.450	1.150	74.00	1.071	0.240	3.600
	ST2	26.38	160	331	253	4.340	2.090	24.58	1174	47.76	1221	4.400	0.429	0.921	77.00	0.975	0.112	2.190
	Mean	29.32	157	275	208	4.010	2.080	21.84	976	44.26	1020	3.680	0.440	1.036	77.50	1.023	0.176	2.900
17 July 14	ST3	24.28	233	642	851	16.05	3.390	24.68	2774	113	2887	8.090	0.309	1.080	69.00	0.779	0.051	1.930
	ST4	2.650	583	1130	1045	25.92	7.631	18.33	3831	209	4040	4.150	0.438	1.090	76.00	1.600	0.6091	4.690
	ST5	2.110	158	452	797	18.16	5.660	25.14	2590	103	2693	11.42	0.215	1.290	28.00	2.960	0.811	6.490
	Mean	9.680	325	741	898	20.04	5.560	22.72	3065	142	3207	7.887	0.321	1.150	57.67	1.780	0.490	4.370
	ST6	1.530	347	1049	1178	30.53	5.170	22.63	4644	206	4850	11.57	0.297	1.040	67.00	4.670	0.252	6.220
	ΣMean	14.87	272	637	714	16.45	4.334	22.41	2632	120	2752	7.098	0.356	1.095	65.17	2.009	0.345	4.190
	s.d	14.24	170	378	457	10.96	2.210	3.000	1488	73.60	1560	3.810	0.096	0.122	18.63	1.520	0.299	1.955
	ST1	33.09	693	2765	1013	62.00	60.00	10.86	6439	593	7032	1.950	0.750	1.740	11.55	0.939	0.280	2.540
	ST2	30.02	314	2556	849	50.53	30.67	15.56	4832	310	5142	2.450	1.230	2.200	10.23	1.032	0.782	3.180
	Mean	31.56	504	2661	931	56.27	45.34	13.21	5636	452	6087	2.20	0.990	1.970	10.89	0.986	0.531	2.860

Continued

1 Nov 14	ST3	25.67	253	1371	230	34.61	17.27	11.43	2445	214	2659	1.720	1.330	2.440	14.65	1.420	0.259	3.850
	ST4	14.97	742	1108	525	36.84	11.15	8.280	2544	307	2851	1.310	0.870	2.260	66.54	1.570	0.933	2.980
	ST5	13.7	386	1088	412	35.78	14.12	13.36	2623	196	2819	2.420	0.757	2.040	27.18	1.014	0.537	2.660
	Mean	18.11	460	1189	389	35.74	14.18	11.02	2537	239	2776	1.820	0.986	2.250	36.12	1.334	0.576	3.163
	ST6	10.91	326	1011	379	37.50	14.97	10.35	2393	231	2624	2.670	0.740	2.070	21.78	0.775	0.341	3.510
	ST7	4.450	469	1866	798	47.24	16.67	19.39	4841	250	5091	4.580	0.590	2.110	28.08	0.536	0.241	1.900
	Mean	7.680	398	1439	589	42.37	15.82	14.87	3617	241	3858	3.625	0.665	2.090	24.93	0.656	0.291	2.705
	ΣMean	18.97	454	1680	601	43.50	23.55	12.74	3731	300	4031	2.443	0.896	2.122	25.72	1.041	0.482	2.945
	S.d	10.69	192	730	288	10.20	17.23	3.730	1626	136	1736	1.050	0.300	0.220	19.38	0.360	0.278	0.650
31 Jan 15	ST1	31.81	259	397	231	11.32	3.390	14.76	1101	74.62	1176	4.290	0.572	1.640	76.40	1.016	0.008	1.740
	ST2	25.86	150	281	165	9.340	1.700	14.95	758	50.70	809	4.310	0.600	2.180	88.20	0.400	0.004	0.920
	Mean	28.84	205	339	198	10.33	2.540	14.86	930	62.66	993	4.300	0.586	1.910	82.30	0.708	0.006	1.330
	ST3	9.520	147	174	133	9.210	1.330	12.56	565	45.01	610	2.810	0.460	2.240	111	0.394	0.023	2.050
	ST4	7.910	219	240	170	11.45	2.060	14.11	850	60.22	910	3.320	0.383	2.490	106	2.360	0.037	2.170
	ST5	21.44	295	350	409	15.13	3.520	18.59	1631	87.74	1719	5.210	0.270	1.450	83.80	0.446	0.009	1.350
	Mean	12.96	220	255	237	11.93	2.303	15.09	1015	64.32	1080	3.780	0.371	2.060	100	1.070	0.023	1.860
	ST6	5.630	335	561	537	20.79	4.610	20.06	2309	115	2424	5.190	0.307	1.290	72.67	1.520	0.008	4.090
	ST7	1.260	656	1523	793	26.32	9.700	23.84	4210	177	4387	4.010	0.570	1.030	67.63	1.039	0.007	1.700
	Mean	3.450	496	1042	665	23.56	7.160	21.95	3260	146	3406	4.600	0.440	1.160	70.15	1.280	0.008	2.890
	Σmean	14.78	294	504	348	14.79	3.759	16.98	1632	87.18	1719	4.163	0.452	1.760	86.53	1.025	0.013	2.003
	s.d	11.54	174	466	246	6.490	2.860	4.000	1284	46.25	1331	0.890	0.135	0.548	16.53	0.725	0.012	1.012
Whole	Range	0.240 - 33.09	27.25 - 693	-84.00 - 3237	-68.38 - 1768	-1.500 - 85.00	-0.900 - 60.00	5.198 - 22.41	344 - 8724	23.50 - 593	368 - 9121	0.690 - 11.57	0.200 - 1.330	0.377 - 4.080	3.610 - 190	-0.400 - 39.55	-0.004 - 8.361	-0.920 - 27.98
	Mean	16.61	275	761	399	21.20	9.333	14.13	2168	160	2328	3.650	0.622	1.662	52.99	8.504	0.781	7.564
	s.d	12.23	142	510	289	14.30	7.842	3.198	1346	88.66	1442	1.872	0.242	0.449	21.29	4.446	1.028	3.937

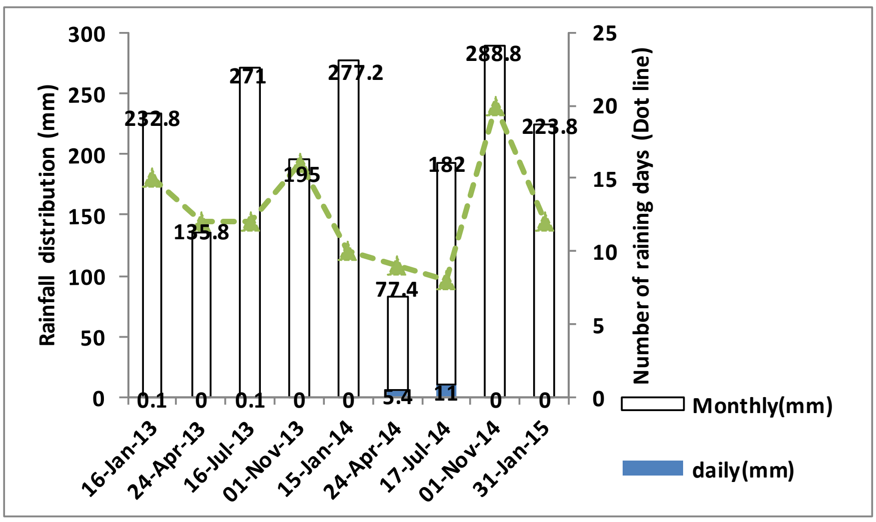


Figure 2. Rainfall distribution data contains monthly, daily and number of raining day adopted from the MMD year 2013 to year 2015 at Kuantan Station. Fortunately on 24 April 2014 and 17 July 2014 have only shown daily rainfall (blue color).

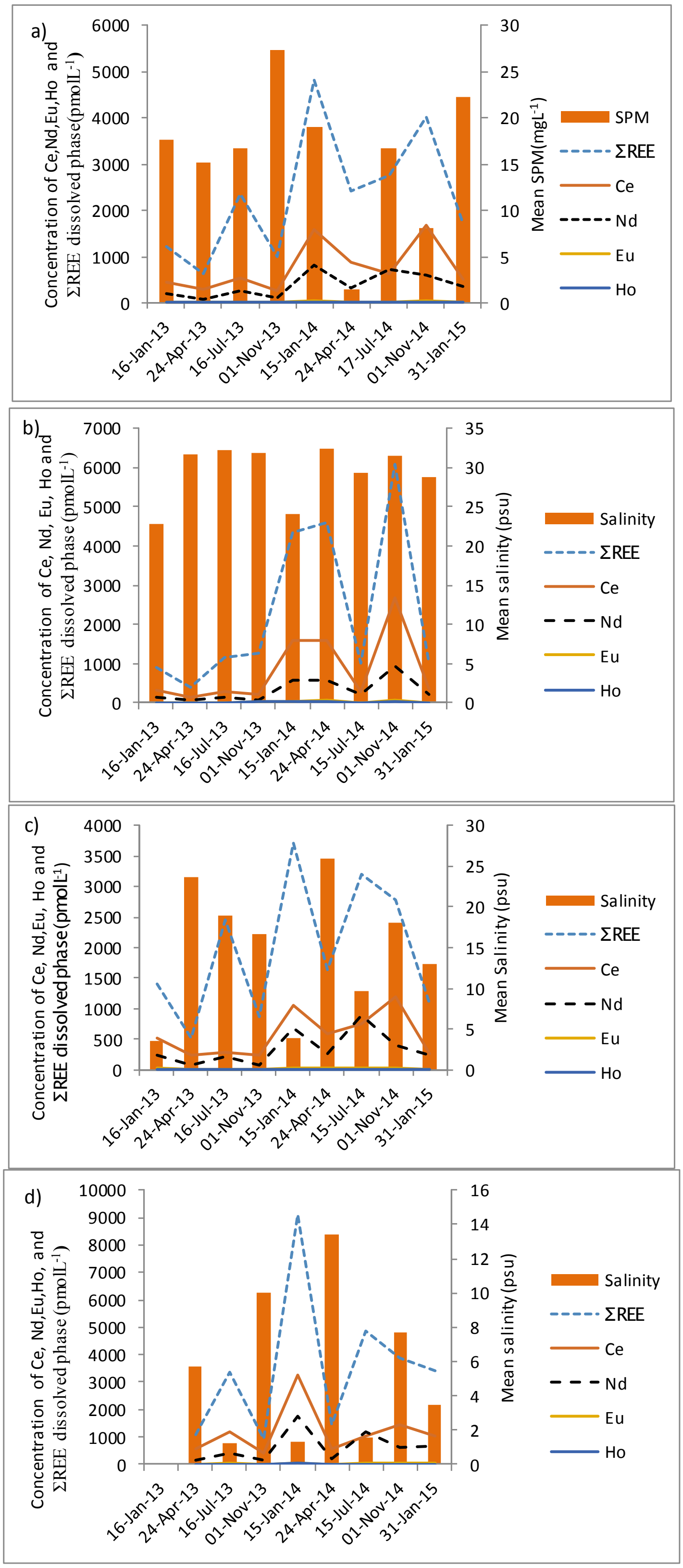


Figure 3. Diagram of relation of mean concentration of Ce, Nd, Eu, Ho and ΣREE dissolved toward sampling seasons and (a) mean concentration of SPM, (b) mean salinity in coastal zone, (c) estuarine zone and (d) river zone.

The same scenarios were also observed by the other elements e.g., Ce, Nd, Eu and Ho in the coastal zone especially during monsoon events because of the abundant inorganic carbon in seawater during semidiurnal tides and the tidal pump phenomenon [20]. The river zones occupied by station 2 and station 3 have a water depth of less than 5 m along the sand bar. Hence, these stations experienced higher deposition of sediments and particles from the sand bar (**Figure 1**; **Table 1**). However, the fluctuating rainfall events affected the concentrations of suspended particulate matter in surface river discharges (**Figure 3(a)**).

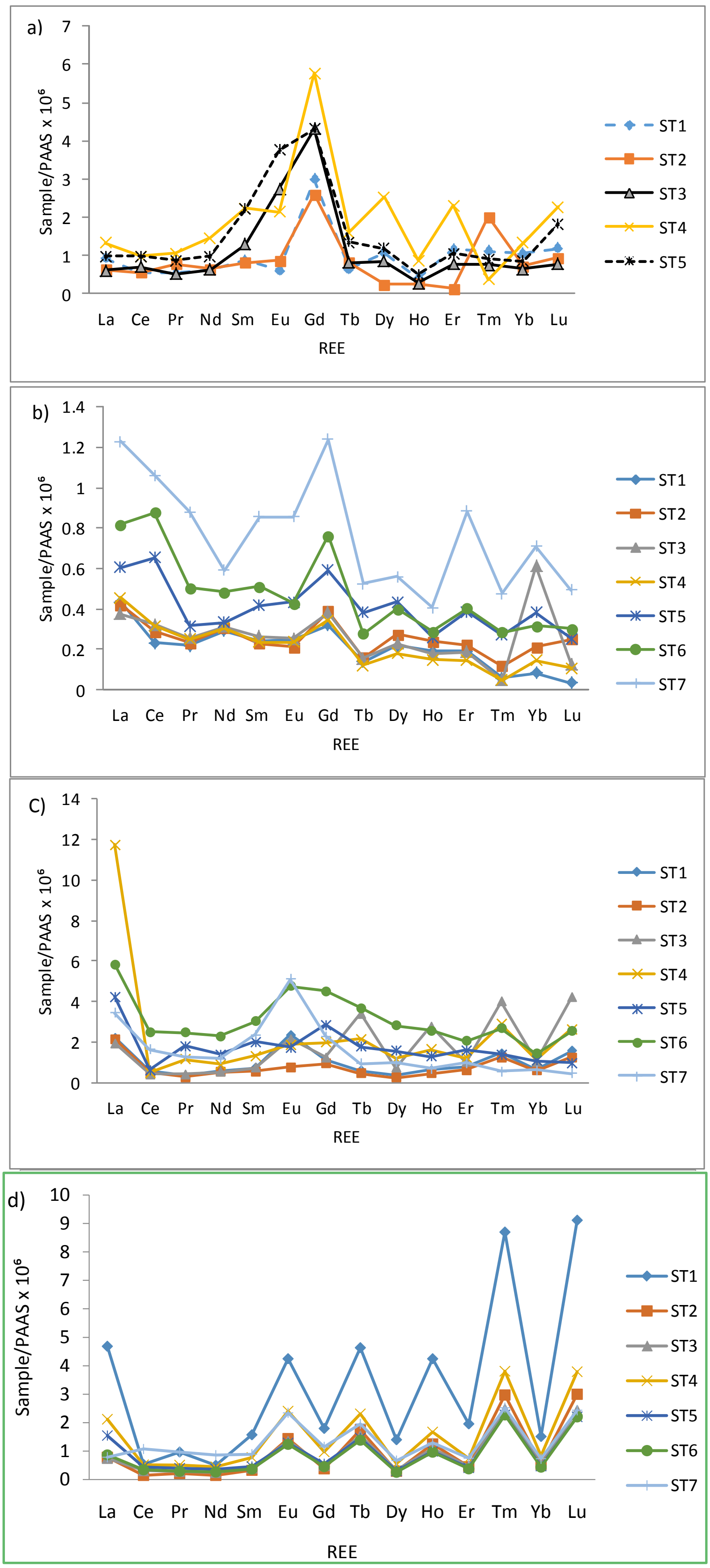
According Agaki (2013) [21], it was indicated that the silicate or opal has the potential as an REE scavenger in the seawater column. Notwithstanding the presence of abundant biogenic SiO_2 also has a linear relationship with organic matter or organic carbon in the estuarine or marine environment. The distribution of silicate originated from terrestrial sources and detrital minerals from lithogenous and hydrogenous phases [22]. Sungai Balok is surrounded by a mangrove habitat and studies of estuarine fluxes by using REE proxies around the world found that the tropical river flux of trace metals in the dissolved phase have a high possibility of being from rainfall runoff and submarine groundwater discharge [23]. The concentration of biogenic SiO_2 from the wet season in January 2014 to dry season during April 2014 and July 2014 (**Table 3**) found that the high distribution of REEs in January 2014 was associated with the increase of biogenic SiO_2. While the decrease of REE concentrations in April 2014 and July 2014 were associated with decreasing biogenic SiO_2, which is known as an REE scavenger in the marine environment.

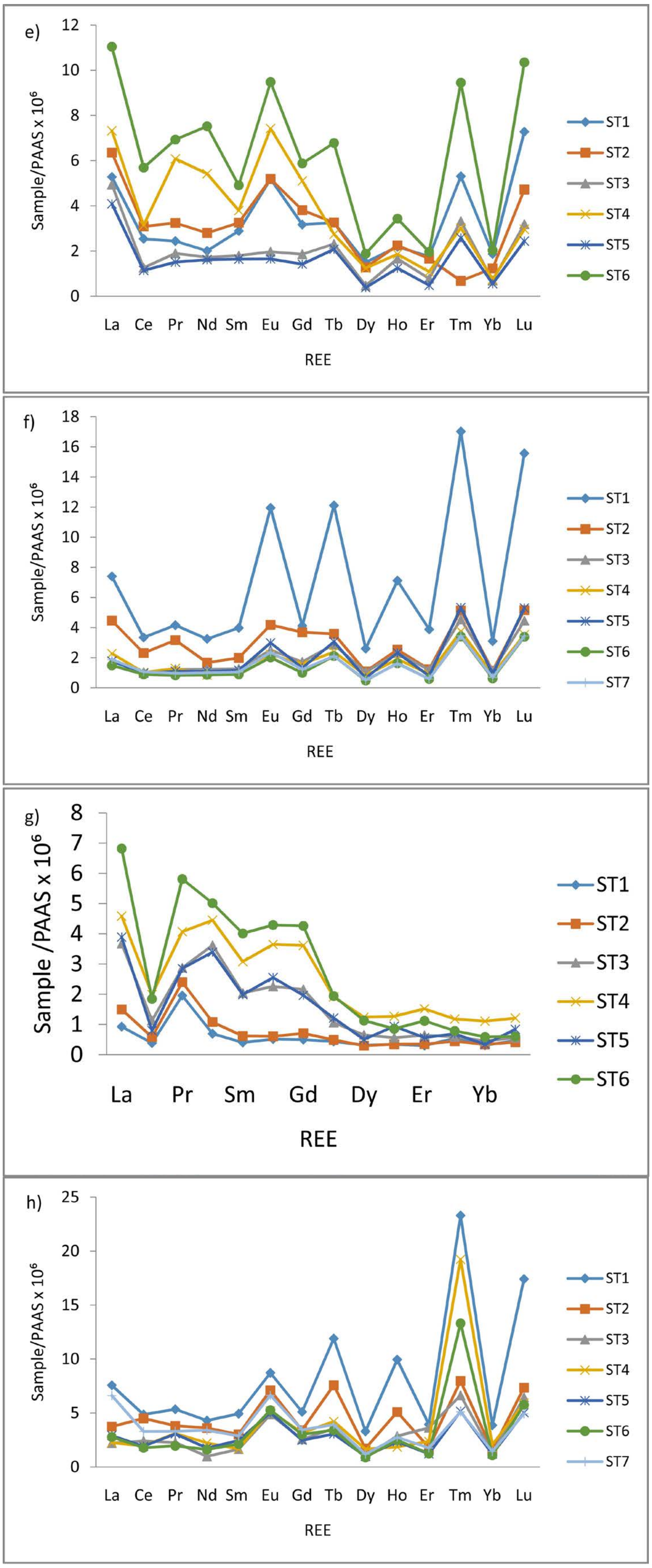
The high ratio value of HREEs in the dissolved phase especially at station ST 1 (**Figure 4(h)**) might be because of inorganic carbonate from seawater. The inorganic carbonate has been depicted as the greatest positive factor of Tm anomaly (>28) with similar patterns in **Figures 4(d)-(f)**. A positive Gd anomaly in **Figure 4(a)** & **Figure 4(b)** with a range value of lower than 6 also indicated more natural freshwater from the hinterland to the study location [24], and the high positive anomaly value (>5) of Pr in **Figure 4(d)** was due to regenerated particle matter from surface sediments and nutrients [25]. Similarly, researchers have already discussed the enrichment pattern of MREEs and the enrichment pattern of MREE in this sampling locations also showed abundant positive anomaly of Eu (e.g., **Figure 4(a)**; **Figure 4(e)** and **Figure 4(i)**) (*i.e.*, [3] [14]).

Table 3. Concentrations level of dissolved biogenic SiO_2, (ppm) in Sungai Balok at various times of sampling.

Period	Sampling zones		
	River	Estuarine	coastal
15-Jan-14	5.30 ± 0.17	5.09*	0.55 ± 0.06
24-Apr-14	5.16 ± 0.17	4.95*	0.39 ± 0.05
17-Jul-14	3.50 ± 0.48	1.86 ± 0.23	0.13 ± 0.03

(*) single reading without replicate.


a)
Sample/PAAS x 10⁶
0
1
2
3
4
5
6
7
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
REE
ST1
ST2
ST3
ST4
ST5
b)
Sample/PAAS x 10⁶
0
0.2
0.4
0.6
0.8
1
1.2
1.4
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
REE
ST1
ST2
ST3
ST4
ST5
ST6
ST7
C)
Sample/PAAS x 10⁶
0
2
4
6
8
10
12
14
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
REE
ST1
ST2
ST3
ST4
ST5
ST6
ST7
d)
Sample/PAAS x 10⁶
0
1
2
3
4
5
6
7
8
9
10
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
REE
ST1
ST2
ST3
ST4
ST5
ST6
ST7


e)
Sample/PAAS x 10⁶
12
10
8
6
4
2
0
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
REE
ST1
ST2
ST3
ST4
ST5
ST6
f)
Sample/PAAS x 10⁶
18
16
14
12
10
8
6
4
2
0
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
REE
ST1
ST2
ST3
ST4
ST5
ST6
ST7
g)
Sample /PAAS x 10⁶
8
7
6
5
4
3
2
1
0
La Pr Sm Gd Dy Er Yb
REE
ST1
ST2
ST3
ST4
ST5
ST6
h)
Sample/PAAS x 10⁶
25
20
15
10
5
0
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
REE
ST1
ST2
ST3
ST4
ST5
ST6
ST7

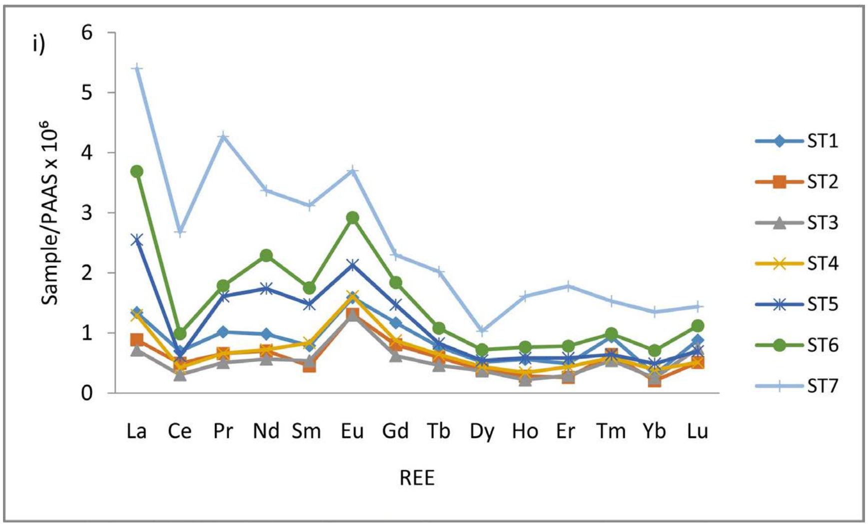


Figure 4. REE normalized PAAS patterns (a) Jan 2013; (b) April 2013; (c) July 2013; (d) Nov 2013; (e) Jan 2014 (f) April 2014; (g) July 2014; (h) Nov 2014; (i) Jan 2015.

3.2. Terrestrial Input Proxies

Sungai Balok drains towards the southern South China Sea (sSCS) and the effect of salt water intrusions is higher compared to the west coast of Peninsular Malaysia *i.e.*, the Straits of Malacca [26]. The dissolved REEs have a strong affinity to particulate REEs and reactive particles in the marine environment [1]. Terrestrial runoff occurring during heavy rainfall may have brought an abundance of terrigenous detrital matter and particulate organic matter into the river and ocean environments. The negative statistical correlation was observed between particles and rainwater, which means particles such as dust, particulate matter and volatile gases were scavenged during wet deposition [27].

Ce species is dominant in certain conditions due to abundance among the REEs and in the environment it can be applied to determine the oxidation and reduction stage of cerium either Ce/Ce* < 1 and Ce/Ce* > 1 by Ce^{4+} and Ce^{3+}, respectively. The adsorption of dissolved REEs will be scavenged to surface sediments, and the negative Ce anomaly (Ce/Ce*) along the stations ranging from 0.2 to 1.33 showed that oxidation process of stage IV occurred at Sungai Balok. Researchers Nozaki *et al.* (1997) [28] and Sholkovitz *et al.* (1999) [2] also explained the adsorption process could be detected by process of Ce oxidation in the marine environment. However, De Baar (1983) [29] noted that in the presence of oxygen, the seabed regeneration can reduce the Ce (IV) to Ce (III) especially in the river and terrestrial area. Sungai Balok also showed that the positive Ce/Ce* was abundant at the stations in the river and estuarine zones (*i.e.*, ST3 to ST7) ranging from 1.0 to 1.33. The highest was recorded at ST7 in November 2013 and might be due to the weathering process as shown by lowest ratio value of Y/Ho (9.247 ± 4.026) and high contents of Mn (3.543 ± 2.74 $\mu mol \cdot L^{-1}$) compared to other sampling periods. According to Sholkovitz (1992) [4], the increased Mn oxide acts as the catalyst for supplying oxygen demand in surface water in order to maintain the dissolved REE in III charge. The moderate and strong significant correlations were determined among Ce, Eu, Nd and Ho, however, strong correlation ($p < 0.001$) was observed between LREE and total REE indicating chemical charge of REE (III) has strong binding affinity among dissolved REE members.

Europium (Eu) is a suitable terrestrial dust proxy available from the lithogenic sources such as igneous, granite rock, dust, hydrothermal and volcanic land (e.g., [4] [14]). The Eu anomaly has the ability to evaluate the lithogenic input through the ratio of Y/Ho [30], where the ratio Y/Ho < 55 in the study suggests a lot of freshwater input in the Sungai Balok river system (**Figure 5**) especially during the Northeast monsoon. The values of Eu anomalies also fluctuated in all the zones ranging 0.489 to 3.3 in the coastal zone, 0.836 to 2.767 in the estuarine zone, and 0.755 to 2.68 in the river zone (**Table 2**) which might be due to the fluctuation of monsoon events in the sSCS region.

The ratio of La/Yb_N is a common indicator to determine the enrichment of LREE over HREE [31] and the ratio was also used as a lithogenic proxy in Tokyo Bay by Takahashi and Noriki (2007) [6]. Meanwhile, the fluctuating rainfall events in the East coast of Peninsular of Malaysia have significant statistical correlation ($p = 0.05$) with La/Yb_N ratio and the ratios were high in January 2014 and July 2014 with values of 6.43 ± 2.47 and 7.098 ± 3.81, respectively. The overall ratios of La/Yb_N ranged between 0.69 to 11.57 throughout the sampling periods. The high amount of monthly rainfall distribution in January 2014 increased the soil humidity and dissolution of dissolved REE. Hence, the highest total concentration of 4825 ± 2460 pmol·L^{-1} was observed during that time. However, the high ratio of La/Yb_N in July 2014 (*i.e.*, lower monthly rainfall) might be due to sudden rainfall during the sampling day along with concentration of 11 mm per day as reported by MMD (2015) [32] (**Figure 2**).

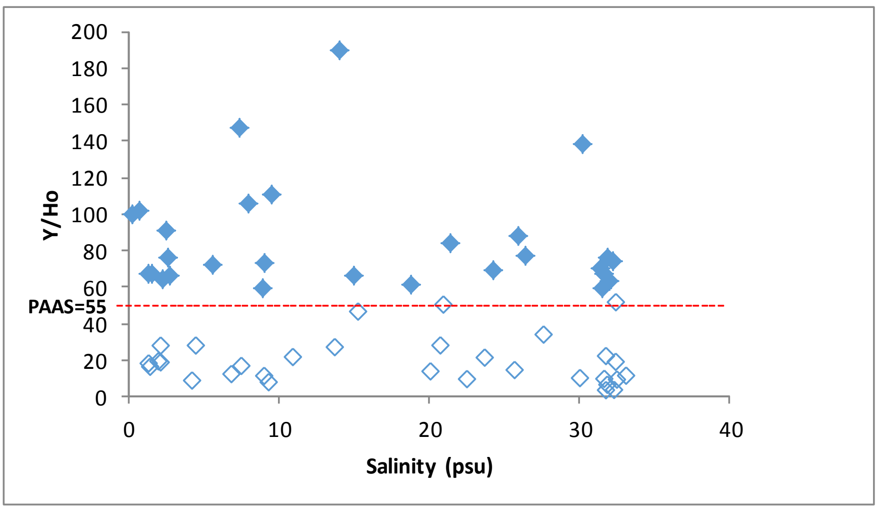


Figure 5. Diagram showing the relationship between dissolved Y/Ho ratio and salinity. Open diamond is below PAAS which distributed from 31 samplings while closed diamond upper that PAAS which distributed from 28 sampling points in the Sungai Balok.

3.3. Rare Earth Elements Budget into the Southern South China Sea

Sungai Balok falls into the southern South China Sea zone [14] and the amount of REEs discharged are still not well documented. Due to the abundance of Ce among REE members, it has been selected for the calculation of river fluxes. The flux of REEs was estimated using formula (1), while an inventory could be developed by formula (2) adopted from the published journal [28]. The inventory and flux of dissolved REEs were estimated using the Ce element in **Table 4** and **Table 5**. By consideration of the residence time of Ce [33] where the value of Ce is 80 years while Nd is 270 years. Due to the unstable nature of Ce, it is not the main choice for the geochemistry scientists to determine the residence time in

Table 4. The inventories of dissolved Ce over three years sampling periods in Sungai Balok.

Date/period	Station	Average C_{ce} ($pmol·L^{-1}$)	Average D* (m)	Inventory ($pmol·cm^{-2}$)
16-Jan-13	St1-St5	433	3.4	147
24-Apr-13	St1-St7	305	3.83	117
16-Jul-13	St1-St7	549	3.83	210
1-Nov-13	St1-St7	276	3.83	106
15-Jan-14	St1-St6	1598	3.67	587
24-Apr-14	St1-St7	865	3.83	331
17-Jul-14	St1-St6	637	3.67	234
1-Nov-14	St1-St7	1680	3.83	643
31-Jan-15	St1-St7	504	3.83	193

*D; Average depth stations. Note: Inventory is obtained from Equation (2); The value of L is converted to cm^3 and m is converted to cm, where 1L is equals to 1000 cm^3 and 1m is equals to 100 cm.

Table 5. The dissolved Ce Fluxes over three years sampling periods in Sungai Balok.

Date/period	$c(ti)$ Average Ce ($pmol·L^{-1}$)	$Q(ti)$ Average Daily river discharged × 10^{-6} ($L·s^{-1}·cm^{-2}$)	$\frac{1}{N}$ Conversion factor ($s·yr^{-1}$)	Fluxes ($nmol·cm^{-2}·yr^{-1}$)
24th April 2013 to 16th July 2013	427	6.887	84 × 86,400	21.34
1st Nov 2013 to 15th Jan 2014	937	6.887	76 × 86,400	39.14
24th April 2014 to 17th July 2014	751	6.887	85 × 86,400	37.98
1st Nov 2014 to 31st Jan 2015	1092	6.887	92 × 86,400	59.78

Note: Period was divided to two seasons which were during monsoon from November to January while after monsoon from April until July of sampling periods. Average Ce is obtained from average concentration within four months. The conversion factors $1/N$ of sampling periods are obtained by calculated the days of sampling period time to value 86400 of second per days. Fluxes is obtained from Equation (1) after entering the value of conversion factor, average daily river discharge and dissolved Ce concentration.

marine, coastal and ocean areas and mostly use the Nd as a proxy. However, from this finding the dissolved REE river flux was identified by measuring the accumulation duration over the sampling period conducted in **Table 5**, but not the remaining dissolved REE or resident at the sampling point.

$$\text{Inventory} = C_{\text{REE}} \times D \tag{2}$$

where, the C is the concentration of dissolved REE ($pmol \cdot L^{-1}$) in the water column, D is the depth of water column (m). Therefore, an inventory could also be produced by multiplication of the C which is concentration of dissolved REE ($pmol \cdot L^{-1}$) in the water column with D which is the depth of water column (m).

The accumulation of dissolved REEs could be represented by the dissolved Nd and Eu fluxes with the overall domination during the Northeast monsoon which was also supported by the previous findings in November 1996 [34] and in August 1997 [13]. Although Nd fluxes were widely used to measure the river and seawater fluxes for dissolved REE deposition, the Eu flux could potentially be used to measure the lithogenic input into the river system. According to Nozaki *et al.* (1999) [28] the South China Sea is the origin of the fluvial and coastal input that has been feeding the Northern South China Sea and also the Sulu Sea at a rate of 1.7 Nd $pmol \cdot cm^2 \cdot yr^{-1}$, while other Nd flux contributions were also 3.2 $pmol \cdot cm^{-2} \cdot yr^{-1}$ [5] and 1.2 $pmol \cdot cm^{-2} \cdot yr^{-1}$ [35]. Similarly, newer studies on the dissolved Nd flux budget in the Bay of Bengal also reported 1.9 to 6.0 × 10^{-7} $mol \cdot m^{-2} \cdot yr^{-1}$ or 1.9 to 6 $mmol \cdot cm^{-2} \cdot yr^{-1}$ caused by high lithogenic input from the Ganges-Brahmaputra river [8].

The calculated inventories of dissolved Ce in January and November 2014 were 586.5 $pmol \cdot cm^{-2}$ and 643.4 $pmol \cdot cm^{-2}$, respectively (**Table 4**). The results from Sungai Balok might be due to the dilution of river water because of frequent heavy rain during the Monsoon and freshwater discharge during weathering processes the in southern South China Sea. Hence, the river flux deposition increased during both periods of November 2013 to January 2014 and November 2014 to January 2015 along the value of 39.14 $nmol \cdot cm^{-2} \cdot yr^{-1}$ and 59.78 $nmol \cdot cm^{-2} \cdot yr^{-1}$ (**Table 5**). Moreover, the inventory of dissolved Ce also showed a strong correlation with monthly rainfall distribution ($R^2 = 0.52$). This statistical correlation showed the possibility of higher rainfall distributions in November until January that might have caused the increased dissolved Ce flux compared to other periods. Overall the dissolved Ce fluxes over seasons as shown in **Table 5** were greater compare to previous reports from Nozaki *et al.* (1999) [28]. The Nd was used to budget the deposition fluxes in offshore areas and oceans by Yu *et al.* (2017) [8] because of the longer residence time in deep locations *i.e.*, it was estimated about 1.5 - 2.6 years. Therefore, it was not practical to state that where the depth of the river is shallower, the residence time is shortest. Furthermore, according to Greaves *et al.* (1994) [35] the reason to use Nd for estimating flux is because Nd and Sm are good indicators for river evolution. However, most of the tropical rivers are still in pristine condition [36], probably due to wash out by a lot of freshwater and abundant of rainfall. This consequently delivered abundant lithogenic sources especially Al and Ce from crustal and most of the Asean continental parts. Despite the unstable Ce element caused by oxidation and reduction, the study has considered to choose it based on the findings of similar river fluxes assessed by Sholkovit *et al.* (1999) [2] where Eu followed the same behavior of Ce.

According to Sholkovits and Szymczak (2000) [37], the Indonesian archipelagos, Papua New Guinea (PNG), Peninsular Malaysia and Borneo were believed to supply more than 20% of global sediment input into the sea. The island weathering activities explained that the terrestrial sources draining into rivers and the huge river discharges of more than 2×10^{15} $m^3 \cdot s^{-1}$ fold was due to storms and inundation [2]. The PNG and Indonesia archipelagoes were also fed by sources of volcanic and hydrothermal eruptions. Thus, river input has made the fluvial flux amount increase to 1.4×10^{16} $pmol \cdot yr^{-1}$ of Eu or estimated to be about 1.4×10^{10} $pmol \cdot cm^{-2} \cdot yr^{-1}$. These values are greater compared to this present study and might be due to lithogenic and terrigenous volcanic sources around the Indonesian archipelagoes. Furthermore, according to Yu *et al.* (2017) [8], the amount of fluvial fluxes were also affected by biological uptake from organisms such as plankton, process of iron hydroxide co-precipitation and colloidal coagulation in the marine environment and physical factors such as canyons and tidal changing phenomena. However, the abundance of basaltic and granitic rocks [14] along the East Coast of Peninsular Malaysia should be considered for the increased dissolved Ce Fluxes as well as rainfall events that make Sungai Balok unique.

4. Conclusion

The fluctuations of monthly rainfall events directly control the concentration and distribution of REEs in the dissolved phases at sampling locations especially during the Northeast monsoon with the dominant element demonstrated by Ce. The ratio of La/Yb_N in the dissolved phase of REEs was also found to be a suitable proxy for evaluating lithogenic sources during rainfall events. The rainwater runoff along lithogenic sources from terrestrial into the river found $Y/Ho < 55$ that also indicates a large volume of freshwater discharge into the river. The strong significant correlation between Al and Fe also supports the lithogenic sources being actively re-suspended in the water column during water mixing due to the rainfall events. Therefore, the river inventories and fluxes could be estimated through the dominated element of Ce, which is related to the high rainfall distribution during the Northeast monsoon. REEs also have the ability to indicate the changes of monsoon seasons and origins of lithogenic sources in rivers through Ce fluxes and La/Yb_N ratio.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1] Daud, Z. and Mohamed, C.A.R. (2016) A Short Review of the Distribution and Behavior of Rare Earth Elements in the South China Sea. *Pollution Research*, **35**, 25-36.

[2] Sholkovitz, E.R., Elderfield, H., Szymczak, R. and Casey, K. (1999) Island Weathering: River Sources of Rare Earth Elements to the Western Pacific Ocean. *Marine Chemistry*, **68**, 39-57. https://doi.org/10.1016/S0304-4203(99)00064-X

[3] Shynu, R.V., Rao, P., Pratima, M., Kessarkar and Rao, T.G. (2011) Rare Earth Elements in Suspended and Bottom Sediments of the Mandovi Estuary, Central West Coast of India: Influence of Mining. *Estuarine*, *Coastal and Shelf Science*, **94**, 355-368. https://doi.org/10.1016/j.ecss.2011.07.013

[4] Sholkovitz, E.R. (1992) Chemical Evaluation of Rare Earth Elements Fractionation between Colloidal and Solution Phases of Filtered River Water. *Earth and Planetary Science Letter*, **114**, 77-84. https://doi.org/10.1016/0012-821X(92)90152-L

[5] Goldstien, S.J. and Jacobsen, S.B. (1988) Rare Earth Element in River Water. *Earth and Planetary Science Letters*, **89**, 35-47. https://doi.org/10.1016/0012-821X(88)90031-3

[6] Takahashi, N. and Noriki, S. (2007) Rare Earth Elements and Opal/$CaCO_3$ Ratio of Sinking Particles Observed with a Time-Series Sediment Trap at the Mouth of Tokyo Bay. *Journal of Oceanography*, **63**, 941-951. https://doi.org/10.1007/s10872-007-0079-5

[7] Censi, P., Sprovieri, M., Saiano, F., Di Geronimo, S.I., Larocca, D. and Placenti (2007) The Behavior of REEs in Thailand's Mae Klong Estuary: Suggestions from the Y/Ho Ratios and Lanthanidae Tetrad Effects. *Estuarine*, *Coastal and Shelf Science*, **71**, 569-579. https://doi.org/10.1016/j.ecss.2006.09.003

[8] Yu, Z., Colin, C., Douville, E., Meynadier, L. and Bassinot, F. (2017) Seasonal Variations in Dissolved εNd in the Bay of Bengal. *Earth and Planetary Sciences Letters*, **479**, 310-321. https://doi.org/10.1016/j.epsl.2017.09.022

[9] Zhu, Z., Liu, C.-Q., Wang, Z.-L., Liu, X. and Li, J. (2016) Rare Earth Elements Concentrations and Speciation in Rainwater from Guiyang and Acid Rain Impacted Zone of Southwest China. *Chemical Geology*, **44**, 23-34. https://doi.org/10.1016/j.chemgeo.2016.08.038

[10] Ng, S.W.P., Chung, S.L., Robb, L.J., Searle, M.P., Ghani, A.A., Whitehouse, M.J., Oliver, G.J.H., Sone, M., Gardiner, M.J. and Roselee, M.H. (2015) Petrogenesis of Malaysia Granitoids in the Southern Asian Tin Belt. Part 1. Geochemical and Sr-Nd Isotopes Characteristics. *Geological Society of American Bulletin*, **127**, 1209-1237.

[11] Thompson, A., Amistadi, M.K., Chadwick, O.A. and Chorover, J. (2013) Fractionation of Yttrium and Holmium during Basaltic Soil Weathering. *Geochemica at Cosmochimica Acta*, **119**, 18-30. https://doi.org/10.1016/j.gca.2013.06.003

[12] Smith, N.P. (1993) Tidal and Non-Tidal Flushing o Florida Indian Lagoon. *Estuaries*, **16**, 739-746. https://doi.org/10.2307/1352432

[13] Yu, Z., Colin, C., Douville, E., Meynadier, L., Duchamp-Alphonso, S., Sepulcre, S., Wan, S., Song, L., Wu, Q., Xu, Z. and Bassinot, F. (2017) Yttrium and Rare Earth Element Partitioning in Seawater from the Bay of Bengal. *Geochemistry, Geophysics, Geosystems*, **18**, 1388-1403. https://doi.org/10.1002/2016GC006749

[14] Sultan, K. and Shazili, N.A.M. (2009) Rare Earth Element in Tropical Water, Soil and Sediment of Terengganu River Basin, Malaysia. *Journal of Rare Earth*, **27**, 1072-1078. https://doi.org/10.1016/S1002-0721(08)60391-9

[15] Bourg, A.C.M. (1983) Role of Freshwater or Seawater Mixing on Trace Metal Adsorption Phenomenon. In: Wong, C.S., Boyle, E., Bruland, K.W. and Burton, J.D., Eds., *Trace Metal in Sea Water*, Plenum, New York, 195-208. https://doi.org/10.1007/978-1-4757-6864-0_12

[16] Coradin, T., Eglin, D. and Livage, J. (2004) The Silicomolybdic Acid Spectrometric Method and Its Application to Silicate/Biopolymer Interactions Studies. *Spectroscopy*, **18**, 567-576. https://doi.org/10.1155/2004/356207

[17] Benning, R., Schua and Feger, K. (2012) Fluxes of Nitrogen, Phosporus and Dissolved Organic Carbon in the Inflow of the Lehnmuhle Reservoir (Saxony) as Compared to the Streams Draining Three Main Land-Use Types in the Catchman. *Advance in Geosciences*, **32**, 1-7. https://doi.org/10.5194/adgeo-32-1-2012

[18] Department of Irrigation and Drainage (DID) (2011) Review of the National Water Resources Study (2000-2050) and Formulation of National Water Resources Policy. Final Report 12, 444.

[19] McLennan, S.M. (1989) Rare Earth Elements in Sedimentary Rocks: Influences of Provenance and Sedimentary Process. *The Mineralogy Society of America*, **21**, 169-200. https://doi.org/10.1515/9781501509032-010

[20] Wolanski, E., Williams, D. and Hanert, E. (2006) The Sediment Trapping Efficiency of the Micro-Tidal Daly Estuary, Tropical Australia. *Estuarine, Coastal and Shelf Science*, **69**, 291-298. https://doi.org/10.1016/j.ecss.2006.04.023

[21] Agaki, T. (2013) Rare Earth Elements (REE)-Silicic Acid Complexes in Seawater to Explain the Incorporation of REEs in Opal and the Leftover REEs in Surface. New Interpretation of Dissolved REE Profiles. *Geochimica et Cosmochimica Acta*, **113**, 174-192. https://doi.org/10.1016/j.gca.2013.03.014

[22] Tanaka, K., Akagawa, F., Yamamoto, K., Tani, Y., Kawabe, I. and Kawai, T. (2007) Rare Earth Element of Lake Baikal Sediment: Its Implication for Geochemical Response Climate to Climate Change during Last Glacial/Interglacial Transition. *Quaternary Sciences Reviews*, **26**, 1362-1368. https://doi.org/10.1016/j.quascirev.2007.02.004

[23] Johannesson, K.H. and Burdige, D.J. (2007) Balancing the Global Oceanic Neodymium Budget: Evaluating the Role of Groundwater. *Earth and Planetary Sciences Letter*, **253**, 129-142. https://doi.org/10.1016/j.epsl.2006.10.021

[24] Kulaksiz, S. and Bau, M. (2007) Contrasting Behavior of Anthropogenic Gadolinium and Natural Rare Earth Elements in Estuaries and the Gadolinium Input into the North Sea. *Earth and Planetary Sciences Letters*, **260**, 361-371. https://doi.org/10.1016/j.epsl.2007.06.016

[25] Lerche, D. and Nozaki, Y. (1998) Rare Earth Elements of Sinking Particulate Matter in Japan Trench. *Earth and Planetary Science Letters*, **159**, 71-86. https://doi.org/10.1016/S0012-821X(98)00066-1

[26] Bujang Saili, N.A. and Mohamed, C.A.R. (2014) Behavior of ^{210}Po and ^{210}Pb in Shallow Water Region of Mersing Estuary, Johor, Malaysia. *Environment Asia*, **7**, 7-18.

[27] Ambe, Y. and Nishikawa, M. (1987) Variations in Different-Sized Water-Insoluble

Particulate Matter in Rainwater. *Atmosphere Environment*, **21**, 1469-1471. https://doi.org/10.1016/0004-6981(67)90095-9

[28] Nozaki, Y., Alibo, D.S., Amakawa, H., Gamo, T. and Hasumoto, H. (1999) Dissolved Rare Earth Elements and Hydrography in the Sulu Sea. *Geochimica et Cosmochimica Acta*, **57**, 2171-2181. https://doi.org/10.1016/S0016-7037(99)00142-8

[29] De Baar, H.J.W. (1983) Marine Geochemistry on REE. PhD Thesis, MIT University, Boston.

[30] Cidu, R., Antisari, L.V., Biddau, R., Buscaroli, A., Carbone, S., Da Pelo, S., Dinelli, E., Vianello, G. and Zannoni, D. (2013) Dynamics of Rare Earth Elements in Water-Soil System: The Case Study of the Pineta San Vitale (Ravenna, Italy). *Geoderma*, **193**-**194**, 52-67. https://doi.org/10.1016/j.geoderma.2012.10.009

[31] Han, Z., Xu, Z., Tang, Y. and Zhang, G. (2009) Rare Earth Element Patterns in the Karst Terrain of Guizhou Province, China: Implication for Water/Particle Interaction. *Aquatic Geochemistry*, **15**, 457-484. https://doi.org/10.1007/s10498-009-9061-8

[32] Malaysian Meteorological Department (MMD) (2015) Rekod Data Meteorologi di Stesen Meteorologi Kuantan dari Januari 2013 hingga Januari 2015 (In-Bahasa Malaysia).

[33] Goldberg, E.D., Koide, M., Schmitt, R.A. and Smith, R.H. (1963) Rare Earth Distributions in the Marine Environment. *Journal of Geophysical Research*, **68**, 4209-4217. https://doi.org/10.1029/JZ068i014p04209

[34] Nozaki, Y., Lerche, D., Alibo, D.S. and Snidvongs, A. (2000) The Estuarine Geochemistry of Rare Earth Elements and Indium in the Chao Phraya River, Thailand. *Geochimica et Cosmochimica Acta*, **64**, 3983-3994. https://doi.org/10.1016/S0016-7037(00)00473-7

[35] Greaves, M.J., Statham, P.J. and Elderfield, H. (1994) Rare Earth Element Mobilization from Marine Atmospheric Dust to Seawater. *Marine Chemistry*, **46**, 255-260. https://doi.org/10.1016/0304-4203(94)90081-7

[36] Bau, M., Möller, P. and Dulski, P. (1997) Yttrium and Lanthanides in Eastern Mediterranean Seawater and Their Fractionation during Redox-Cycling. *Marine Chemistry*, **56**, 123-131. https://doi.org/10.1016/S0304-4203(96)00091-6

[37] Sholkovits, E.R. and Szymczak, R. (2000) The Estuarine Geochemistry of Rare Earth Element; Comparison of the Amazon, Fly Sepik and the Gulf of Papua System. *Earth and Planetary Science Letters*, **179**, 299-309. https://doi.org/10.1016/S0012-821X(00)00112-6