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RARE EARTH ELEMENTS DISTRIBUTION CHARACTERISTICS IN DISSOLVED AND PARTICULATE FRACTION, AND IN SEDIMENT OF BRUNEI BAY, BORNEO

(Ciri-Ciri Taburan Unsur Nadir Bumi dalam Fraksi Terlarut dan Partikulat, dan Sedimen di Teluk Brunei, Borneo)

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Abstract

The rare earth element (REE) concentrations in the Bay of Brunei were measured in the riverine, main bay area and the South China Sea. The abundance of REE in dissolved, particulate and sediment decreased from light REE (LREE) > medium REE (MREE) > heavy REE (HREE). The ΣREE concentrations were higher in January 2014 as compared to July 2013 in river and estuary sampling sites in all matrices, but more so in the particulate fraction. LREE was found to be highly enriched over HREE in sediment with La/Yb of 22.3 in July 2013 and 14.9 in January 2014. LREE enrichment occurred to a lesser degree in particulate fraction in seawater with La/Yb in the range of 11.7 to 12.8 in July 2013 and 8.4 to 10.6 in January 2014. In the dissolved fraction, LREE was enriched in July 2013 with La/Yb of 3.3 – 3.5 but in January 2014, during the wet Northeast Monsoon season, LREE was depleted with La/Yb of 0.48 in bottom water and 0.74 in surface water. Enhanced scavenging by the higher SPM content entering the bay during the wet season is thought to be the cause of the removal of LREE from the dissolved fraction.

Keywords: rare earth element, dissolved, particulate, sediment, La/Yb

Abstrak

Kepekatan unsur nadir bumi (REE) di Teluk Brunei diukur di kawasan sungai, kawasan teluk dan Laut China Selatan. Kepekatan REE dalam bentuk terlarut, partikulat dan sedimen berkurang dari REE ringan (LREE)> REE sederhana berat (MREE)> REE berat (HREE). Kepekatan ΣREE lebih tinggi pada bulan Januari 2014 berbanding pada bulan Julai 2013 di kawasan sungai dan muara di dalam semua jenis sampel tetapi lebih banyak lagi dalam pecahan partikulat. Didapati LREE sangat diperkaya dengan HREE dalam sedimen dengan La/Yb bernilai 22.3 pada bulan Julai 2013 dan 14.9 pada Januari 2014. Pengkayaan LREE berkurangan di dalam fraksi partikulat di dalam air laut dengan La/Yb bernilai antara 11.7 hingga 12.8 pada bulan Julai 2013 dan 8.4 hingga 10.6 pada bulan Januari 2014. Dalam fraksi terlarut, LREE diperkayakan pada Julai 2013 dengan La/Yb bernilai dari 3.3 - 3.5 tetapi pada Januari 2014, semasa musim Monson Timur Laut yang berkadar hujan yang tinggi, LREE rendah dengan nilai La/Yb 0.48 di air dasar dan 0.74 di permukaan air. Peningkatan penyingkiran oleh kandungan SPM yang lebih tinggi yang memasuki teluk semasa musim hujan dicadangkan sebagai penyebab penyingkiran LREE dari fraksi terlarut.

Kata kunci: unsur nadir bumi, terlarut, partikulat, sedimen, La/Yb

Introduction

The concentrations of rare earth elements (REEs) in seawater and sediment, and comparisons of their dissolved and particulate fractions, may be useful in pollution studies of other elements due to their strong binding to particulates and sediment. As they are tightly correlated with trace metals in sediments, changes in the relative proportions of metals to REEs may indicate anthropogenic influence. The heavy rare earth elements (HREEs) are strongly complex and more stable in solution form, thus facilitating comparisons between the proportions of light rare earth elements (LREEs) and HREEs as another tool for understanding the chemistry of REEs in seawater.

Comparisons of chondrite normalized data may reveal fractionation changes between the different environmental media as a result of variation in physico-chemical characteristics in the aquatic environment. Very little information is available in the context of the Malaysian marine environment. However, REEs have been studied in the freshwater environment of the Terengganu River basin by Sultan and Shazili [1]. Comparison of REEs in Kenyir Lake, Terengganu River and Terengganu River estuary found that the total dissolved solids dominantly control the distribution of dissolved REEs, since it was observed that the concentration of dissolved REEs systematically increased with distance from the upstream towards the downstream. Rezaee et al. [2] has carried out research on REEs in the marine surface sediment off Malaysian waters. The chondrite-normalized REEs show that the sedimentation pattern along Malaysian waters signify the anthropogenic activities as well as the natural processes. Another study carried out by Rezaee et al. [3] found that the chondrite-normalized REEs show the enrichment of LREEs and flat depletion of HREEs in the Malaysian marine sediment.

The Brunei Bay environment is rather complex, with many rivers supplying freshwater from pristine as well as agriculturally and urban developed regions in Sarawak, Sabah and Brunei; and possible anthropogenic sources of metals and REEs from a port, and industrial activities on Labuan Island. In this study, the concentrations of REEs in seawater dissolved (<0.45μm), in particulate fractions and in sediment were measured in Brunei Bay, with the objective of determining the extent of variations in REE concentrations and fractionation between the different fractions during the dry season in July 2013 and during the wet Northeast Monsoon season in January 2014.

Materials and Methods

Five sampling trips were carried out in the period of 10^{th} – 12^{th} May 2013, 26^{th} June 2013 – 2^{nd} July 2013, 10^{th} – 12^{th} October 2013, 7^{th} – 18^{th} January 2014 and 4^{th} – 7^{th} April 2014. Samples were collected at both coastal and transect stations during July 2013 and January 2014. For May 2013, October 2013 and April 2014, the samples were collected at coastal stations only. The investigated area extended from Menumbuk to Limbang of the Malaysian coastline. Seventeen coastal stations were selected along the Brunei Bay coastline and riverine (Figure 1), nine stations were selected surrounding the Labuan Island, noted as Labuan stations, and twenty-two stations were selected in a grid remarked as the transect stations. Water samples were collected at both surface and bottom waters at all transect stations, whilst at the coastal stations, the samples were collected at the surface water column only.

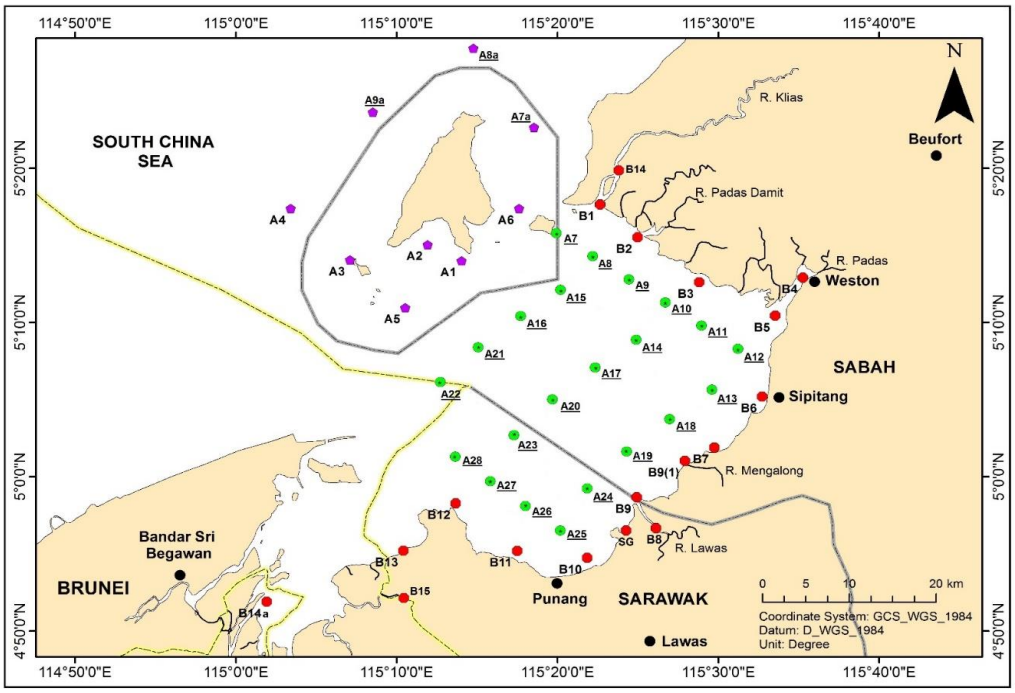

Figure 1. Map of the sampling locations of Brunei Bay, Borneo

Laboratory preparation

All equipment for sampling and sample preparation was thoroughly cleaned with dilute nitric acid and rinsed with ultrapure water before use. Chelex-100 column was prepared using Chelex-100 (sodium form, mesh size of 100-200, powder form, Bio-Rad Laboratories). Polytetrafluoroethylene (PTFE) columns containing Chelex-100 resin were prepared for REE pre-concentration. 50 mL of 2.5 M nitric acid was passed through the column to rinse out all contaminants, followed by 50 mL of deionized water to remove the excess nitric acid. Ammonia solution (50 mL 2M) was then passed through the column, followed by 50 mL of deionized water. Finally, the column was buffered with 20 mL of 1M ammonium acetate (pH 5.3) buffer that had been previously purified using Chelex-100 resin [4, 5]. Solvents, deionized water, buffer, eluent and samples were forced through the column using a peristaltic pump (Masterflex L/S Variable-Speeds Digital Drives) and C-Flex tubing (L/S 14) at a flow rate of 2 mL/min [6]. All procedures were carried out in a Class-100 laminar flow hood to ensure the process is free from contamination. Concentrations of the REEs were measured by an Inductively Coupled Plasma Mass Spectrometer (ICPMS - Perkin Elmer Elan 9000) in a Class-1000 clean room with a Class 100 hood under which the ICPMS was sited.

Sample collection

Duplicate water samples were collected by hand for surface samples and Niskin water sampler for bottom water, and placed in acid washed polyethylene (PE) bottles. The samples were filtered through a 0.45 µm PTFE membrane under a modified closed laminar flow hood equipped with a Class-100 air purifier on the same day. The water samples were then preserved with 2 mL of 65% nitric acid and sealed individually inside PE bags. Suspended particulate matter retained on the PTFE membrane (particulate fraction) was stored inside an acid washed PE container and sealed inside a PE zip lock bag individually. Both samples were kept at low temperature for transportation to the laboratory. Surface sediment was collected using a Ponar grab. The top 5 cm of the sediment was sampled using a plastic scoop. Samples were sealed inside a double layer of PE zip lock bags, kept at low temperature prior to the transportation to the laboratory and kept frozen in a freezer at the laboratory. Water quality parameters including suspended particulate matter were measured with a multiparameter water quality meter (YSI).

Sample treatment and analysis
All procedures in the laboratory were carried out under a Class-100 laminar flow hood in order to prevent contamination.

Dissolved REEs in water sample
Pre-concentration of elements is frequently required owing to their inherent low level in the water samples. Additionally, elements pre-concentration also functions to remove the high concentration of alkali and alkaline earth metal ions in seawater that interferes in the instrumental analysis [7]. Chelex-100 chelating resin was used to pre-concentrate the REEs which were in the "exchangeable fraction" [8, 9]. Chelex-100 operational efficiency is well defined; based on the contact time of the resin with the sample, resin volume as well as sample flow rate can be measured [8, 10].

The REEs pre-concentration procedure was carried out under a Class-100 laminar flow hood to avoid contamination. Filtered water samples were adjusted to pH 5.3, and a total of 200 mL of water sample was passed through a Chelex-100 column at a flow rate of 2 mL/min. Columns were washed with 25 mL of ammonium acetate (previously cleaned by Chelex-100 resin) to remove the saline matrix [11, 12] The elements were finally eluted with 10 mL of 2M nitric acid with a flow rate of 2 mL/min and kept in 15 mL centrifuge tubes at 4°C before analysis using ICP-MS was conducted. This pre-concentration step resulted in a concentration factor of 20 times the initial amount. Blanks were measured to check for metal contamination.

Particulate REEs in water sample
All procedures were done under a Class-100 laminar flow hood to minimise contamination. Suspended particulate matter retained by 0.45 µm PTFE membrane filter was dried to constant weight under Class-100 laminar flow hood. Afterwards, the PTFE filter membrane was digested with 1.5 mL of mixed acids (nitric acid, hydrochloric acid and hydrofluoric acid in the ratio 3:3:1). The mixture was then digested in a closed Teflon bomb under oven heating for 7 hours at a temperature of 120°C and left to cool to room temperature [7, 13]. The sample volume was made up to 10 mL with deionized water. Blanks were measured to check for elemental contamination. Digested samples were kept in centrifuge tubes at 4°C before conducting ICP-MS measurements.

REEs in sediment sample
The method used to digest sediment samples was adopted from [14, 15]. Sediment samples were dried at 60 °C under oven heating. The dried sediments were then crushed mildly using a pestle and mortar. Approximately 0.05g of the bulk sediment was weighed in a Teflon bomb vessel and 1.5 mL of mixed acids (nitric acid, hydrochloric acid and hydrofluoric acid in the ratio 3:3:2) were added. The mixture was digested under oven heating for 7 hours at a temperature of 120 °C, then left to cool until room temperature. The sample volume was made up to 10 mL with deionized water. Blanks were measured to check for metal contamination. Digested samples were kept in centrifuge tubes at 4 °C before analysis using ICP-MS was done.

Accuracy and precision
The internal standard method was applied to validate the REEs in dissolved, particulate and surface sediment samples using 5 ppb and 10 ppb of Multi-elements Calibration Standard 2, 10 µg/mL (17 elements in 5% nitric acid). Chelex-100 column blanks were carried out by using 200 mL of deionized water as the water sample, followed by the same steps as for water samples for dissolved metal analysis. The particulate metal blanks were prepared by digesting clean PTFE membrane filters without any sediment sample. Sediment blanks consisted of acid digestion in the PTFE vessels without sediment. Besides assessing the quality control, blanks were used to determine the limit of detection [16]. Good recoveries were achieved for REEs in the dissolved (95.8 ± 4.11% for 5ppb; 94.5 ± 4.47% for 10 ppb) and particulate fraction (97.8 ± 3.64% for 5 ppb; 96.6 ± 4.16% for 10 ppb) and sediment (96.1 ± 3.63% for 5 ppb; 97.8 ± 3.86% for 10 ppb). The detection limits ranged from 0.2 ng/L for Tm to 2.2 ng/L for La in the dissolved fraction. In the particulate fraction, detection limits ranged from 0.16 µg/kg for Tm to 48 µg/kg for La, and in sediment, from 1.0 µg/kg for Tm to 40.9 µg/kg for La.

Results and Discussion

Dissolved rare earth elements

The average, standard deviation, minimum and maximum data of dissolved REEs are recorded in Table 4. The highest dissolved elements found in May 2013 water samples were Cerium (Ce), Praseodymium (Pr), Neodymium (Nd), Samarium (Sm), Europium (Eu), Gadolinium (Gd), Terbium (Tb), Dysprosium (Dy), Erbium (Er) and Ytterbium (Yb). Dissolved Holmium (Ho), Thulium (Tm) and Lutetium (Lu) were higher in the surface water of January 2014 while dissolved La concentration was highest in July 2013 in the bottom waters (Figure 2). Dissolved Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu concentrations were lowest in October 2013 while dissolved La, Ce, Pr and Nd concentrations were lowest in bottom waters in January 2014 (Figure 2).

Table 4. Mean, standard deviation and range (in parentheses) concentration of dissolved REEs and Al for the different sampling periods (µg/L)

Element (µg/L)	July 2013 surface	July 2013 bottom	January 2014 surface	January 2014 bottom
La	0.127 ± 0.112 (0.039 - 0.692)	0.186 ± 0.191 (0.035 - 0.972)	0.060 ± 0.119 (0.013 - 0.831)	0.027 ± 0.008 (0.017 - 0.052)
Ce	0.102 ± 0.068 (0.043 - 0.452)	0.125 ± 0.123 (0.035 - 0.618)	0.093 ± 0.133 (0.014 - 0.827)	0.038 ± 0.017 (0.023 - 0.100)
Pr	0.097 ± 0.213 (0.020 - 1.352)	0.074 ± 0.121 (0.025 - 0.677)	0.051 ± 0.112 (0.012 - 0.788)	0.020 ± 0.006 (0.012 - 0.036)
Nd	0.462 ± 1.246 (0.079 - 7.821)	0.255 ± 0.201 (0.099 - 0.970)	0.119 ± 0.140 (0.028 - 0.950)	0.068 ± 0.015 (0.034 - 0.104)
Sm	0.075 ± 0.031 (0.009 - 0.135)	0.087 ± 0.141 (0.013 - 0.797)	0.115 ± 0.140 (0.054 - 1.041)	0.082 ± 0.014 (0.055 - 0.110)
Eu	0.054 ± 0.020 (0.019 - 0.119)	0.071 ± 0.139 (0.022 - 0.776)	0.059 ± 0.136 (0.017 - 0.964)	0.033 ± 0.009 (0.016 - 0.051)
Gd	0.199 ± 0.588 (0.016 - 3.699)	0.109 ± 0.122 (0.034 - 0.651)	0.103 ± 0.132 (0.038 - 0.965)	0.071 ± 0.017 (0.041 - 0.110)
Tb	0.045 ± 0.022 (0.018 - 0.116)	0.059 ± 0.141 (0.018 - 0.776)	0.058 ± 0.144 (0.017 - 1.018)	0.027 ± 0.005 (0.015 - 0.037)
Dy	0.040 ± 0.037 (0.001 - 0.209)	0.054 ± 0.116 (0.001 - 0.640)	0.081 ± 0.118 (0.023 - 0.861)	0.051 ± 0.014 (0.021 - 0.078)
Ho	0.006 ± 0.004 (0.001 - 0.019)	0.008 ± 0.026 (0.000 - 0.141)	0.017 ± 0.043 (0.004 - 0.302)	0.009 ± 0.002 (0.006 - 0.013)
Er	0.052 ± 0.021 (0.014 - 0.103)	0.063 ± 0.119 (0.001 - 0.666)	0.078 ± 0.143 (0.028 - 1.032)	0.053 ± 0.010 (0.036 - 0.079)
Tm	0.004 ± 0.002 (0.001 - 0.010)	0.005 ± 0.013 (0.001 - 0.072)	0.013 ± 0.034 (0.003 - 0.238)	0.006 ± 0.001 (0.003 - 0.009)
Yb	0.038 ± 0.028 (0.000 - 0.118)	0.053 ± 0.127 (0.000 - 0.697)	0.081 ± 0.140 (0.016 - 1.008)	0.056 ± 0.014 (0.029 - 0.092)
Lu	0.003 ± 0.002 (0.000 - 0.009)	0.004 ± 0.014 (0.001 - 0.076)	0.010 ± 0.028 (0.002 - 0.197)	0.004 ± 0.001 (0.001 - 0.006)
Al	10.4 ± 10.4 (0.122 - 36.6)	10.6 ± 21.8 (0.124 - 115)	110 ± 446 (24.7 - 3132)	26.4 ± 10.3 (19.3 – 76.9)

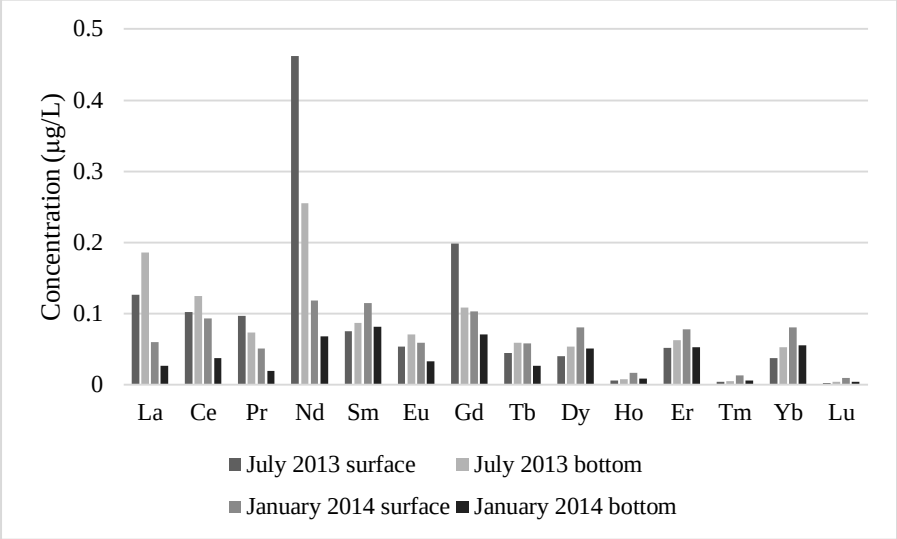

Figure 2. The average concentration of dissolved REEs in Brunei Bay

Particulate rare earth elements

Particulate Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu were highest in average concentrations in October 2013, while particulate La was the only element recorded with the highest average concentration in surface water in January 2014 (Figure 3). This finding is likely influenced by the northeast monsoon period since significant correlation ($p < 0.05$) of the above mentioned REEs with high concentration of suspended particulate matter and acidic water pH was observed. During the northeast monsoon, the western region of Borneo Island receives heavy rainfall [17, 18]. Such occurrence leads to a flushing out of a high load of suspended particulate matter into the sea, which reduced the water pH value. The average, standard deviation, minimum and maximum concentration of particulate REEs are recorded in Table 5. Overall, bottom water samples in July 2013 had the lowest average concentrations of all particulate REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) as compared to other sampling periods.

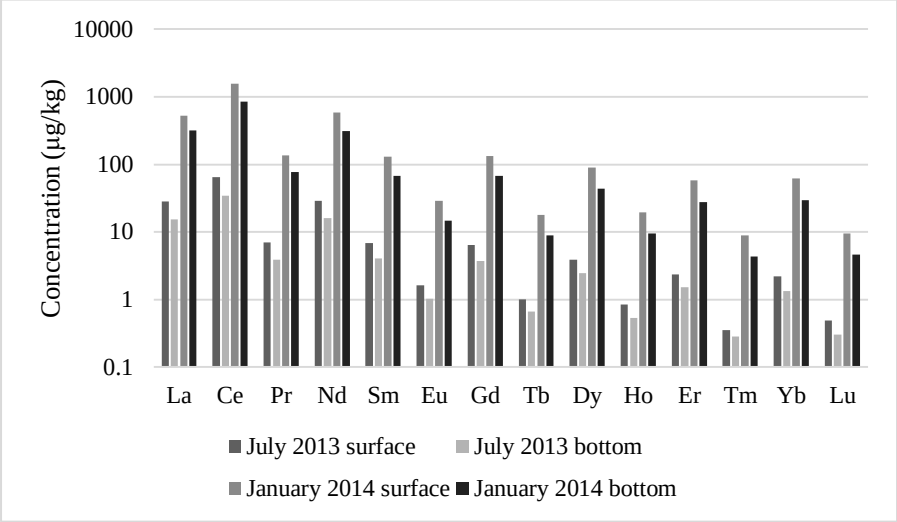

Figure 3. The average concentration of particulate REEs in Brunei Bay

Table 5. Mean, standard deviation and range (in parentheses) concentration of particulate REEs and Al for the different sampling periods (µg/g)

Element (µg/kg)	July 2013 Surface	July 2013 Bottom	January 2014 Surface	January 2014 Bottom
La	28.0 ± 40.9 (2.35 - 187)	15.5 ± 11.1 (3.09 - 106)	527 ± 414 (72.2 - 2100)	315 ± 222 (57.4 - 1060)
Ce	64.5 ± 94.4 (4.82 - 404)	34.1 ± 26.0 (7.35 - 245)	1556 ± 1348 (135 - 4612)	850 ± 920 (106 - 4328)
Pr	7.06 ± 10.5 (0.585 - 47.8)	3.85 ± 2.73 (0.945 - 27.3)	137 ± 109 (13.8 - 388)	76.8 ± 66.7 (10.8 - 296)
Nd	28.7 ± 43.5 (1.66 - 201)	16.1 ± 11.0 (2.78 - 112)	582 ± 486 (55.2 - 1944)	311 ± 267 (44.1 - 1264)
Sm	6.89 ± 9.26 (1.25 - 40.6)	4.08 ± 2.29 (0.97 - 22.9)	129 ± 106 (12.9 - 374)	67.4 ± 61.7 (8.64 - 253)
Eu	1.62 ± 2.08 (0.220 - 8.99)	1.02 ± 0.556 (0.245 - 4.71)	28.8 ± 23.4 (2.74 - 82.9)	14.7 ± 13.2 (1.86 - 57.2)
Gd	6.37 ± 8.78 (0.983 - 38.4)	3.68 ± 2.18 (0.947 - 19.5)	132 ± 107 (18.2 - 389)	66.9 ± 60.8 (9.71 - 262)
Tb	1.00 ± 1.16 (0.222 - 5.04)	0.661 ± 0.317 (0.181 - 2.53)	17.8 ± 14.3 (2.73 - 51.8)	8.86 ± 7.89 (1.58 - 36.4)
Dy	3.86 ± 5.29 (0.161 - 25.0)	2.44 ± 1.32 (0.570 - 11.7)	90.3 ± 76.7 (13.1 - 285)	43.8 ± 41.1 (6.19 - 189)
Ho	0.847 ± 0.98 (0.155 - 4.74)	0.536 ± 0.267 (0.153 - 2.31)	19.7 ± 16.8 (2.86 - 63.8)	9.55 ± 8.76 (1.66 - 41.1)
Er	2.33 ± 2.80 (0.364 - 12.1)	1.53 ± 0.846 (0.367 - 6.76)	57.7 ± 51.1 (7.90 - 196)	27.6 ± 26.0 (4.56 - 122)
Tm	0.352 ± 0.391 (0.030 - 2.13)	0.282 ± 0.130 (0.054 - 0.940)	8.98 ± 7.92 (1.27 - 31.1)	4.36 ± 4.09 (0.728 - 19.4)
Yb	2.18 ± 2.61 (0.255 - 12.4)	1.32 ± 0.818 (0.177 - 6.25)	62.5 ± 57.2 (7.29 - 227)	29.7 ± 29.2 (3.79 - 136)
Lu	0.490 ± 0.546 (0.092 - 2.87)	0.304 ± 0.177 (0.081 - 0.989)	9.50 ± 8.65 (1.36 - 34.0)	4.59 ± 4.43 (0.561 - 20.9)
Al	362 ± 529 (31.4 - 2249)	202 ± 157 (56.0 - 737)	6915 ± 8220 (211 - 19732)	1858 ± 2889 (210 - 14211)

Rare earth elements in surface sediment

The average, standard deviation, minimum and maximum data of REEs in surface sediment are recorded in Table 6. Similar to the dissolved and particulate REEs, the distribution of the highest and lowest REEs in surface sediment was more consistent as compared to metals in surface sediment samples. Overall, the highest average concentration of REEs (including La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) was found in the October 2013 samples.

Surface sediment samples during April 2014 recorded the lowest in average values of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho and Er, while Tm, Yb and Lu were lowest in May 2013 (Figure 4). This finding is influenced by the southwest monsoon period, since significant correlation ($p<0.05$) of the above mentioned REEs with lowest concentration of suspended particulate matter was observed. During the southwest monsoon, the western region of

Borneo Island experiences relatively drier weather [17, 18]. Such occurrence leads to a significantly low load of suspended particulate matter flushed out into the sea.

Table 6. Mean, standard deviation and range (in parentheses) concentration of REEs (µg/g) and Al (%) in surface sediment from all sampling sites

Element (µg/g)	**July 2013**	**January 2014**
La	11.7 ± 5.01 (3.61 - 20.3)	15.6 ± 13.9 (0.133 - 42.8)
Ce	25.5 ± 10.4 (7.47 - 42.5)	41.2 ± 33.9 (0.006 - 106)
Pr	2.91 ± 1.14 (0.829 - 4.73)	4.17 ± 3.50 (0.006 - 10.9)
Nd	11.7 ± 4.45 (3.30 - 18.7)	17.0 ± 14.2 (0.025 - 45.0)
Sm	2.34 ± 0.868 (0.639 - 3.65)	3.40 ± 2.74 (0.006 - 8.97)
Eu	0.502 ± 0.190 (0.142 - 0.782)	0.746 ± 0.567 (0.003 - 1.88)
Gd	2.38 ± 0.881 (0.685 - 3.90)	3.55 ± 2.86 (0.008 - 9.02)
Tb	0.264 ± 0.093 (0.080 - 0.404)	0.392 ± 0.301 (0.000 - 0.990)
Dy	1.32 ± 0.447 (0.422 - 2.04)	2.11 ± 1.57 (0.002 - 5.27)
Ho	0.229 ± 0.076 (0.077 - 0.365)	0.390 ± 0.289 (0.000 - 0.958)
Er	0.614 ± 0.205 (0.200 - 0.953)	1.11 ± 0.834 (0.003 - 2.76)
Tm	0.082 ± 0.026 (0.030 - 0.131)	0.160 ± 0.120 (0.001 - 0.395)
Yb	0.520 ± 0.165 (0.178 - 0.792)	1.05 ± 0.788 (0.001 - 2.47)
Lu	0.075 ± 0.024 (0.028 - 0.114)	0.152 ± 0.117 (0.000 - 0.380)
Al (%)	3.72 ± 2.04 (0.440 – 6.08)	4.01 ± 2.33 (0.004 – 7.72)

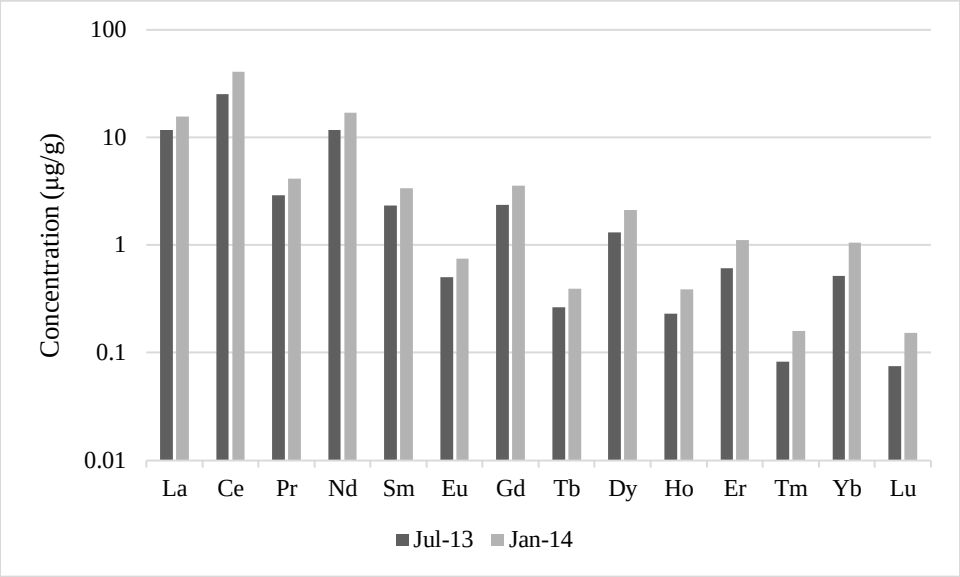

Figure 4. The average concentration of REEs in the surface sediment of Brunei Bay

Rare earth elements (REE) can be used to define the source of contaminants [19] by determining the origin of metals that are closely related to water-sediment interaction, and as geochemical tracers of flow paths of water in water bodies [20]. The partitioning of the aqueous and solid fractions REEs is influenced by pH, temperature, redox as well as selective ligand-complexation of dissolved REE ions in water [21-26].

The average concentration of REEs in Brunei Bay samples are shown in Table 7. The abundance order of REEs in dissolved, particulate and surface sediment decreased from light REE (LREE) > medium REE (MREE) > heavy REE (HREE). Overall, the concentration of LREEs was higher than HREEs for all sampling periods, probably due to high adsorption of LREEs onto clay particles, while HREEs remain dominant in solution. This finding is similar to the findings discovered in the sediment of Yellow Sea, Yangtze River, Florida Bay as well as in the estuarine sediment of east coast of India [27-30]. ΣREE concentration were higher in January 2014 than in July 2013 in river and estuary sampling sites, and especially so in particulate fraction from all sampling sites (Table 7). The majority of the REEs during January 2014 were in the LREE fraction in river, estuary and bay particulate matter while in particulates from the South China Sea off Labuan Island, a significantly lesser number of REEs were in the LREE fraction.

ΣLREE is highly enriched over ΣHREE in sediment and in particulates in July 2013 compared to January 2014 particularly in riverine stations (Table 7), but the difference is less for estuarine, the bay and South China Sea stations. In the dissolved fraction ΣLREE:ΣHREE ratios in the bay area were generally similar to South China Sea stations during both sampling periods.

The La/Yb anomaly is usually applied to determine the ratio between LREE and HREE. Specifically, La/Yb was 22.3 in July 2013 and in January 2014 La/Yb was 14.9 in sediment in riverine stations. In particulate fraction, in surface and bottom water of the bay, La/Yb ranged from 11.7 to 12.8 for July 2013, and from 8.4 to 10.6 in January 2014. A La/Yb of 3.3-3.5 in dissolved fraction in July 2013 indicates much lower enrichment in the dissolved fraction compared to particulate fraction and sediment (Table 9). LREE enrichment relative to HREE has been similarly measured in the Terengganu River Basin, Terengganu [1]. High LREE in the surface sediment results from the high affinity of REE to bind with carbonates. This finding is similar to those found in the surface marine sediment of Malaysian coasts [2, 3, 31].

Table 7. The average concentration of REE in Brunei Bay, Borneo

Sampling period		Dissolved (µg/L)				Particulate (µg/g)				Surface Sediment (µg/g)			
		R	E	B	S	R	E	B	S	R	E	B	S
July 2013	ΣREE	722	1252	904	403	588	538	76	19	48	90	62	18
	ΣLREE	569	1081	803	298	553	506	69	16	46	84	58	17
	ΣMREE	152	346	204	99	48	41	7.05	2.09	2.85	7.00	4.66	1.33
	ΣHREE	153	171	102	105	35	33	6.79	2.32	2.04	5.66	3.24	1.01
	ΣLREE/ ΣHREE	3.7	6.3	2.8	2.8	15.8	15.3	10.2	6.9	22.5	14.8	17.9	15.4
January 2014	ΣREE	806	1800	434	395	5940	7877	2586	560	129	111	92	3.86
	ΣLREE	631	1215	289	263	5443	7230	2388	513	120	103	87	3.53
	ΣMREE	201	543	136	117	466	640	206	48	9.97	8.54	6.76	0.42
	ΣHREE	175	585	146	132	497	647	198	47	8.63	7.48	5.11	0.33
	ΣLREE/ ΣHREE	3.6	2.1	2.0	2.0	11.0	11.2	12.1	10.9	13.9	13.8	17.0	10.7

Note: R - River stations, E - Estuary stations, B - Bay stations, S - South China Sea stations

ΣREE, ΣLREE and ΣHREE concentrations increased by up to ten times in the particulate fraction in January 2014. Interestingly LREE was seen depleted in January 2014 with ratios of La/Yb of 0.48 in bottom water and 0.74 in surface water, although this is not obvious from the ΣLREE: ΣHREE ratio (Table 7). This depletion in LREE indicates dilution by freshwater during the Monsoon rains in January. It also indicates that different chemistries between bottom and surface waters play a significant role in the REE distribution in the dissolved and particulate fraction and in sediment. According to Suhaila and Jemain [17], the northeast monsoon typically sets in over the South China Sea in early November, lasting till early March, which brings in heavy rainfall to the east coast of Peninsular Malaysia and western Sarawak [18].

Normalization of Sm to Nd (Table 8) results in similar Sm/Nd ratios of 0.16-0.34 in the three sample types during July 2013 and January 2014, except for January 2014 where Sm/Nd were close to 1.0 (0.97-1.21). The ratios of Nd/La are close to 1.0 (0.97-1.10) for particulate fraction and sediment in July 2013 and January 2014, whereas Nd is significantly enriched relative to La in the dissolved fraction for both sampling periods. A similar pattern is observed for Er/La with ratios of 0.05-0.11 for particulate fraction and sediment, and significant enrichment of Er over La during January 2014 with ratios of 1.3-1.96.

The SPM concentration in Brunei Bay was highest (32.1 ± 104 mgL^{-1}) in surface water during January 2014 (Table 9), and thus scavenging capacity and dilution by fresh SPM resulted in lower La/Yb in dissolved and particulate fraction compared to the drier conditions in July 2013 (Table 8). Water quality parameters (Table 9) during these two sampling periods showed only a slightly lower pH during January 2014, but a marked reduction in dissolved oxygen was recorded in the surface waters of Brunei Bay. Thus, **Σ**LREE is relatively enriched in the dissolved fraction than in particulate fraction and in sediment, with enrichment in sediment > particulate fraction > dissolved fraction.

In the wet northeast Monsoon season (January 2014 samples) a significantly different pattern in REE distribution is generally observed in the dissolved fraction, particularly with regards to La/Yb, Sm/Nd and Er/La ratios (Table 8). The ratios of Sm/Nd, Nd/La and Er/La in the particulate fraction are similar to values in sediment, indicating that there is no fractionation of REEs in the mineralised form. However, REE ratios in the dissolved fraction differ substantially between the July and January sampling periods, indicating leaching from land sources or increased

scavenging (La/Yb). Ratio of La/Yb is significantly reduced in the dissolved fraction in January 2014, indicating enhanced scavenging of light REEs together with dilution by the higher SPM content (Table 9) from terrigenous sources, as evidenced by the 19-fold increase in Al concentration in particulates (Table 5).

Table 8. REE ratios in Brunei Bay in dissolved and particulate forms and in sediment for the July 2013 and January 2014

		July 2013		January 2014	
		Surface	**Bottom**	**Surface**	**Bottom**
La/Yb	Dissolved	3.34	3.51	0.74	0.48
	Particulate	12.8	11.7	8.43	10.6
	Sediment	22.5		14.8	
$(La/Yb)_{diss}/(La/Yb)_{part}$		0.26	0.30	0.09	0.04
Sm/Nd	Dissolved	0.16	0.34	0.96	1.21
	Particulate	0.24	0.25	0.22	0.22
	Sediment	0.20		0.20	
Nd/La	Dissolved	3.63	1.37	1.98	2.5
	Particulate	1.02	1.04	1.10	0.98
	Sediment	1.00		1.09	
Er/La	Dissolved	0.41	0.33	1.3	1.96
	Particulate	0.08	0.10	0.11	0.09
	Sediment	0.05		0.07	

Comparison of relative REE concentrations in the dissolved phase with those in the suspended particulate matter phase by $(La/Yb)_{dissolved}$:$(La/Yb)_{particulate}$ result in ratios of 0.26 and 0.3, respectively, during the dry season, and 0.09 and 0.04, respectively, in the wet season, indicating the strong influence of riverine input in Brunei Bay on REE chemistry. These values are typical of tropical rivers and indicate relative enrichments of heavy REEs in the suspended load from the formation of carbonate complexes favoured in river water of pH = 8 [32].

Table 9. Mean, standard deviation and range (in parentheses) of water physical parameters of Brunei Bay

Sampling Period	**pH**	**DO (mg/L)**	**Salinity (ppt)**	**Temperature (°C)**	**SPM (mg/L)**
July 2013 (surface)	8.17 ± 0.33 (7.24 - 8.42)	6.05 ± 0.54 (4.72 - 6.95)	26.8 ± 6.97 (0.38 - 31.3)	30.4 ± 0.95 (27.8 - 32.0)	14.8 ± 27 (0.67 - 166)
July 2013 (bottom)	8.17 ± 0.19 (7.89 - 8.39)	3.51 ± 2.03 (0.21 - 5.71)	32.8 ± 0.85 (30.3 - 33.9)	29.6 ± 0.84 (27.6 - 30.8)	11.3 ± 7.68 (4.50 - 45.0)
January 2014 (surface)	7.85 ± 0.54 (6.04 - 8.18)	4.88 ± 1.16 (0.65 - 8.47)	23.2 ± 9.12 (0.03 - 30.7)	28.7 ± 1.57 (24.6 - 30.6)	32.1 ± 104 (4.50 - 679)
January 2014 (bottom)	8.04 ± 0.07 (7.88 - 8.12)	3.68 ± 0.91 (1.32 - 4.69)	33.9 ± 0.78 (31.9 - 34.6)	28.9 ± 0.38 (28.4 - 29.7)	9.69 ± 7.25 (4.50 - 38.3)

Conclusion

Rare earth element concentrations in particulate and sediment fractions showed some differences between the sampling period of July in the dry season and of January in the wet season. However, the dissolved fraction showed similar distributions of ΣLREE:ΣHREE during both sampling periods. Light over heavy REE as determined by La/Yb ratios is significantly reduced in the dissolved fraction in January 2014, indicating enhanced scavenging of light REEs together with dilution by the higher SPM content from terrigenous sources during the wet season.

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