e-Jurnal Sains Nuklear Malaysia, 2021, Vol. 33: 29 – 45
eISSN: 2232-0946

ASSESSMENT OF ELEMENTS IN SURFACE SEDIMENTS OF PERAI RIVER, PENANG USING NEUTRON ACTIVATION ANALYSIS (NAA) TECHNIQUE

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ABSTRACT

This study was to assess the concentration levels of ten elements within the surface sediments collected from upstream to downstream at the main Perai river and one of its subsidiary of Penang. The elemental concentrations were measured using non-destructive nuclear technique of Neutron Activation Analysis (NAA). The average concentration found in the elementals of Antimony (Sb), Arsenic (As), Barium (Ba), Cobalt (Co), Chromium (Cr), Iron (Fe), Scandium (Sc), Uranium (U), Thorium (Th), and Zinc (Zn) was 1.5 ppm, 16.9 ppm, 306.7 ppm, 6.5 ppm, 69.8 ppm, 2.9 %, 11.1 ppm, 11.4 ppm, 37.9 ppm and 244.9 ppm, respectively. Halves of the studied elements namely the As, Sb, U, Th and Zn were found having the mean concentration value greater than the continental crust (CC) value, whilst the others having lower mean concentration as compared to CC value. Correlations among the elements, organic matters and particle sizes were also studied. Five elements namely As, Co, Sc, Th and Zn were found significantly correlated with the iron concentrations and the organic matters content whilst the correlation between elements and particle sizes were unclear. Overall, the study shown that the enrichment appeared to be severe for As, moderately severe enriched for elements Sb, Th, U and Zn while no enrichment was found for elements Ba, Co, Cr and Sc. Human development activities such as industries and urbanization were believed to be the main contribution to the enrichment of elements.

Keywords: Elements, surface sediment, Perai river, neutron activation analysis, enrichment factor

INTRODUCTION

Environmental processes are complex in nature where interactions occur both within the biosphere and the abiotic environment and between them (Humbird, 2019). In marine environment, they cannot be remedied without taking into account the ecological interdependence of the oceans, the coastal areas and the freshwater systems associated with them (Jeleff, 1999). Environmental processes and ecological systems are strongly influenced by social and economic systems and, in turn, influence by them. A high proportion of the world's population lives in coastal areas of the country, and many of the people derive benefit from the marine and coastal resources, such as from employment that linked with coastal and maritime activities, and also from the coastal recreational opportunities (Burke et al., 2001). However, population pressure, consumption patterns, and increasing demands for space and resources and combined with the poor economic performance and impoverishment of a large part of the global population that undermine the sustainable use of oceans and coastal areas, and of their resources. Globally, both the environmental problems of the coastal areas and the oceans, and their causes, have

remained largely unchanged for several decades. Although there have been some notable successes in addressing problems caused by some forms of marine pollution, and in improving the quality of certain coastal areas, but on a global scale, marine environmental degradation still continued and even intensified in many places. Marine pollution stemming from land-based sources and activities has been of predominant concern nowadays (UNEP, 2019; Williams, 1996; Williams & Davis, 1995).

Marine ecosystem received input from terrestrial mainly through the rivers. River is natural water flow, usually is the fresh water that flow towards ocean, sea, lake or other rivers. The water quality status of rivers in Malaysia has always been a cause for concern for various authorities, the government agencies, as well as the public at large. Human development activities such as industries, urbanization, water transportation and others brought to water pollution. Rivers in Malaysia are generally considered to be polluted with coherent examples such as Juru river in Penang, Klang river in Selangor and Segget river in Johor. One even can deduce that something is not right with the current water quality condition of these rivers just by the physical observation alone (Zainudin, 2010).

Pollutants such as heavy metals released in the river water are considered as serious inorganic pollutants that can be accumulated in sediments and the aquatic food chain (Islam et al., 2017; Li et al., 2017). These can give adverse effects to the aquatic life (Elias et al., 2012; Yi et al., 2011). Water, sediment and biota significantly play an important role in the assessment of the level of pollution, degree of contamination as well as toxicology effects (Elias et al., 2018b; Kumar et al., 2017; Yin et al., 2011).The major sources of inorganic pollutants that originated from anthropogenic sources are for example coming from agriculture activities, animal waste, constructions, domestic sewage, industrial emissions, milling and mining and petroleum activities (Pandey & Singh, 2017; Zhu et al., 2011).

Nowadays, there are many techniques that can be used for elemental analyses and for this study, nuclear technique of Neutron Activation Analysis (NAA) was used. NAA is a versatile and non labour intensive analytical technique. More importantly, special sample preparations, such as digestion or extractions, are not required for this technique, and therefore the NAA method is considered as non-destructive testing method, i.e., the integrity of the sample is not changed by the addition of any foreign materials before sample irradiation. Thus, the problem of reagent introduced contaminants is completely avoided (Elias et al., 2014). Besides this, NAA method is also fast and convenient, and it has the capability of analyses multi-elements and provides highly sensitivity down to sub-picogram concentration levels (IAEA, 1990). The physical phenomenon upon which NAA is based is on the properties of the nucleus, radioactivity and the interaction of radiation with matter. The neutron source released from reactor interacts with target nucleus (samples such as soil, sediment or plant) by non-elastic collision; where a compound nucleus is formed in highly excited state, and a target nucleus (new nucleus) become radioactive and later get de-excited by emitting decay gamma rays (IAEA, 1990). The intensities of the emitted gamma rays which can be quantified using Gamma spectrometry system are then proportional to their concentrations inside the sample.

As Perai river is surrounded by dense populations and multiple industries, waste water released from these human activities may be flown into the river. The purpose of this study is to assess the concentration of several elements (As, Ba, Co, Cr, Fe, Sb, Sc, Th, U, and Zn) in the surface sediments of Perai River, Penang, Malaysia by using the non-destructive nuclear technique of Neutron Activation Analysis. Enrichment factor (EF) for these elements were calculated and discussed in this paper.

MATERIALS AND METHODS

Collection and pre-preparation of samples

Surface sediments were collected on 26th–27th July 2018 using a Ekman™ grab sampler, as shown in Fig. 1, from upstream towards downstream at the Perai river and one of its subsidiary rivers. Nine stations were selected from the main river while three stations were from the subsidiary river. Physical parameters such as temperature, pH, salinity, dissolved oxygen (DO) and total dissolved solid (TDS) of the river waters were also measured as supporting parameters at each sampling station. Description of key activities at sampling stations were given in Table 1. Approximately one (1) kg of sediment was collected and placed into HDPE plastic bag and refrigerated for further analysis. Back in laboratory, small portions of wet samples were taken for particle analysis while remaining sediments were dried in an oven at 80 °C (IAEA, 2003) until constant weight, then fine ground using a Rocklabs™ grinder mill to obtain homogeneous powders of less than 200 mesh (74 μm) size prior further few analyses.

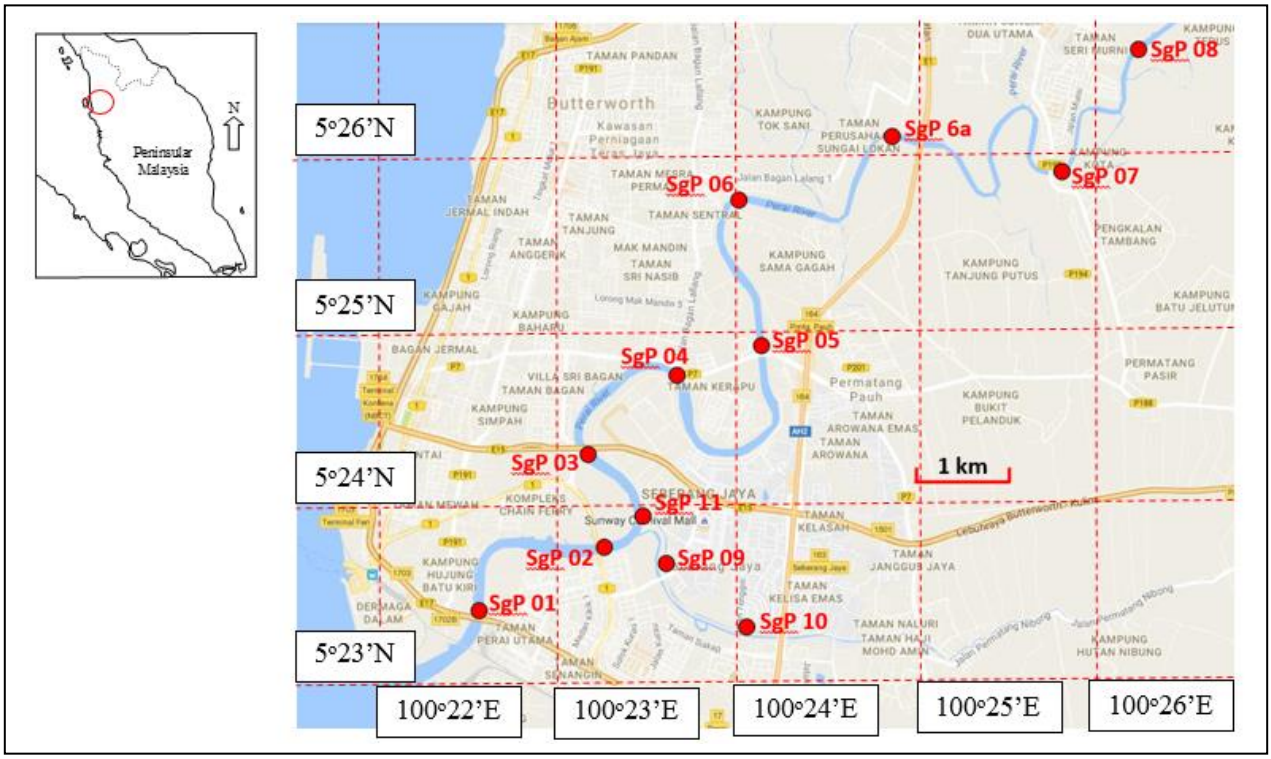


Figure 1: Sampling location

Table 1: Key activities at sampling stations of Perai River

River	Location	Station code	Description of industries activities
Main river	Upstream	SgP 08	Agricultural plantation
		SgP 07	Fishermen boats rest area, seafood restaurants
		SgP 06a	Scrap material warehouse
		SgP 06	Housing areas, domestic waste
		SgP 05	Recreational area
		SgP 04	Shop lots and next to main road
		SgP 03	Industrial areas
		SgP 02	Recreational area
	River mouth	SgP 01	Heavy industries, cargo containers storage yard
Subsidiary river	Upstream	SgP 10	Recreational area
		SgP 09	Pump house and water door
	River mouth	SgP 11	Several scattered factories

Physical parameters

Physical parameters for water at each sampling station were measured simultaneously by using a YSI™ 556 MPS multiprobe meter before the collection of sediment. Data measured included the temperature, pH, salinity, dissolved oxygen and total dissolved solid.

Particle size analysis

Particle size composition in the wet sediment samples were analysed by using Microtrac™ X100 laser diffraction. Particles were characterized into the fractions of sand (> 63 um), silt (4–63 um) and clay (< 4 um) using the Udden–Wentworth scale developed by Krumbein (Blair & McPherson, 1999; Blott & Pye, 2012; Krumbein & Aberdeen, 1937).

Loss on Ignition

Loss on Ignition (LOI) analysis is used to obtain a rough estimation of the organic matter content (% OM) inside a soil/sediment sample. It does not involve the use of any chemicals, but only using the muffle furnace. LOI calculates the % OM by comparing the weight of a sample before and after the soil/sediment has been ignited. Organic matter is oxidized to carbon dioxide and ash at temperatures between ~200 and 500ºC. Weight losses associated with water and carbon dioxide evolutions are easily quantified by recording the sample weights before and after performing the controlled heating (ignition at 550 and 1000ºC) and, in turn, may be correlated to water content, and organic matter as well as the carbonate content (Nelson and Sommers, 1996).

$$\%\,\text{Organic Matter} = \frac{(Weight\ \ Post\ \ 105^{o}C\ \ Dry\ \ sample) - (Weight\ \ Post\ \ 550^{o}C\ \ Ash)}{(Weight\ \ Post\ \ 105^{o}C\ \ Dry\ \ sample)} \times 100 \quad \text{eq (1)}$$

$$\%\,CaCO_3 = \frac{(Weight\ \ Post\ \ 550^oC\ \ Ash) - (Weight\ \ Post\ \ 1000^oC\ \ Ash)}{(Weight\ \ Post\ \ 105^oC\ \ Dry\ \ sample)} \times 2.274 \times 100 \qquad \text{eq (2)}$$

where 2.274 = 100.088 / 44.009 = molecular weight $CaCO_3$ / molecular weight of CO_2.

Elemental analysis

The powdered samples which weighted to approximately 0.1 g were then stored separately in the heat-sealed polyethylene vials in preparation for irradiation. Certified reference material (CRM), IAEA-Soil-7 was used as quality control material. The results of samples were accepted when the values obtained for the reference material fell within the 95% confidence interval as mentioned in the certificate. All samples and reference materials were irradiated with a thermal neutron flux of 4.0×10^{12} n.cm^{-2}.s^{-1} bombarded using the TRIGA Mark II research reactor which operating at 750 kW using pneumatic transport facility. The radiation processes of up to 6h at the rotating rack were performed. After irradiation, cooling times for the decay processes were ranged from 2 to 4 days before performing the first counting, and 3 to 4 weeks after that, for the second counting using the prior calibrated gamma spectrometry. The isotope of radionuclides been measured and other information were tabulated in Table 2 (Ashraf et al., 2018; Elias et al., 2018a).

Table 2: The elements and radionuclides measured using Neutron Activation Analysis (NAA) technique

Elements	**Radionuclides**	**[1]Half-life**	**[2]γ-ray Energy (keV)**
As	^{76}As	26.24±0.09 hours	559.1
Ba	^{131}Ba	11.50 ±0.6 days	496.3
Co	^{60}Co	1925.28±0.14 days	1173.2, 1332.5
Cr	^{51}Cr	27.704±0.004 days	320.1
Fe	^{59}Fe	44.490±0.009 days	1099.3,1291.6
Sb	^{122}Sb	2.7238±0.0002 days	564.2
	^{124}Sb	60.20±0.03 days	602.7
Sc	^{46}Sc	83.79±0.04 days	889.3, 1120.5
Th	^{233}Pa	26.975±0.013 days	312.0
U	^{239}Np	2.356±0.003 days	228.2, 277.6
Zn	^{65}Zn	243.93±0.09 days	1115.6

[1]Radionuclides decay data taken from IAEA (IAEA, 2019).
[2]γ-ray energy data taken from IAEA (IAEA, 1990)

The counting process of the mix standard solution, CRM and irradiated samples were performed for one hour each, by using the gamma spectrometry system. The gamma detector was calibrated from low to high energy of gamma ray by using a mix standard solution that comprising of ^{241}Am (59.5 keV), ^{109}Cd (88.0 keV), ^{57}Co (122.1, 136.5 keV), ^{133}Ba (81.0, 302.9, 356.0, 383.9 keV), ^{137}Cs (661.7 keV), ^{60}Co (1173.2, 1332.5 keV) and ^{88}Y (898.1, 1836.1 keV) according to the calibration procedure described earlier [Alnour et al., 2014; IAEA, 1990; Saion et al., 2007].

Enrichment factor (EF)

In order to evaluate possibilities of heavy metals are coming from anthropogenic sources, enrichment factor for each element (EF) was calculated by using the Eq. (3) as described (Abdus-Salam et al., 2019; Elias et al., 2018a):

$$\mathrm{EF} = \frac{(M/R)_{measure}}{(M/R)_{CC}} \qquad \text{eq. (3)}$$

where M is the element of interest, R is the reference element, $(M/R)_{measure}$ is the elemental ratio found in the sample, and $(M/R)_{CC}$ is the elemental ratio present in the continental crust as described by Wedepohl (1995). Iron (Fe) was used as reference element to normalize the trace element concentrations in order to compensate for variations in particle size and mineralogy (Bhuiyan et al., 2010; Loring and Rantala, 1992). Deely and Fergusson (1994) reported that this is due to that the iron distribution is not being related to other elements. Iron usually has a relatively high concentration in the nature (Abrahim & Parker, 2008), and therefore not expected to be substantially enriched from anthropogenic source in estuarine sediment (Niencheski et al., 1994). If an element found in the sediment is originated predominantly from the lithogenous materials, then the EF value will be less than 2.0, whereas if EF is greater than 2.0, it's indicating that the element is of the anthropogenic origin (Szefer et al., 1996). EFs values were classified according to Ayari et al. (2016) as shown in Table 3.

Table 3: The indication status of enrichment factor (Ayari et al., 2016)

Enrichment factor (EF) value	Enrichment status
< 2	no enrichment
between 2 to < 3	minor enrichment
between 3 to < 5	moderate enrichment
between 5 to < 10	moderately severe enrichment
between 10 to < 25	severe enrichment
between 25 to < 50	very severe enrichment
more than 50	extremely severe enrichment

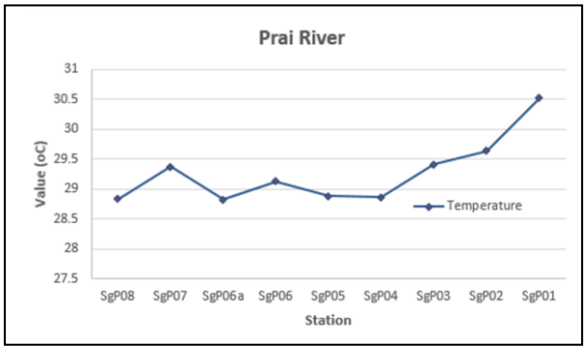
Statistical Analysis

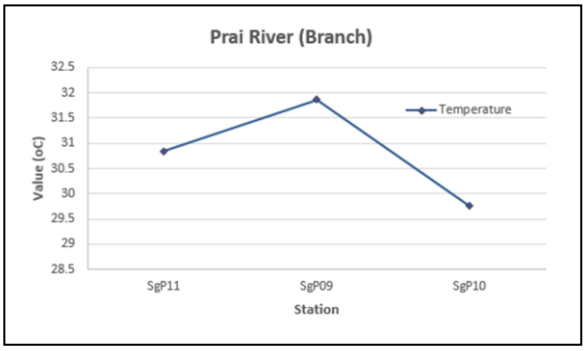
Microsoft™ Office Excel 2013 analysis tools, the Pearson's correlation function and Regression data will be used to analyse data in this study to express the correlation relationship among variables. Pearson's analysis was used to assess the strength and direction of the linear relationships between pairs of variables while the Regression's analysis could determine the significance of the relationships. Correlation between variables would be expressed as significant correlated ($P<0.05$ or $P<0.10$) if their relationships are found to be significance and non-quantitative terminology such as weak, moderate or strong correlations are not been used to discuss the correlations in this article.

RESULTS AND DISCUSSION

Physical parameters

Physical parameters for temperature, pH, salinity, dissolved oxygen and total dissolved solid in Perai river water while sample collection were presented as in Fig. 2. Water temperature very much depends on the surrounding and the sampling time. As the sampling strategy was planned from upstream towards river mouth, the water temperature goes up as the sun rose up, causing an ascending pattern to be observed. Acidity of water measured for pH values varies between 6.4 to 7.1 with an ascending polar for the main Perai river and between 6.6 to 6.9 for its subsidiary indicating that the river water was slightly acidic. The measured pH of the river water were considered to be normal as these values fall within the range of pH range for Class I river water (pH 6.5–8.5) as stipulated under Interim National Water Quality Standards (INWQS) (Zainudin, 2010). Meanwhile, salinity and total dissolved solid values of water were found increasing from upstream towards downstream (from SgP 05 to SgP 01) which were mainly due to the fact that seawater was rising when sampling was performed. Changes in TDS concentrations in natural waters often result from intrusion of seawater, changes to the water balance (by increased water use, by limiting inflow or increased precipitation), or by industrial effluent. Dissolved solids would changes the ionic composition of the water, the individual ions might be toxic and also increased the water salinity. Changes in ionic composition of water could endanger some aquatic species while promote the growth of others. In other words, higher salinity and total dissolved solid in water would affects the freshwater aquatic ecosystem (Weber-Scannell & Duffy, 2007). Finally, the dissolved oxygen (DO) values found at most of the stations in Perai river water generally were low. Adequate dissolved oxygen is necessary for good water quality. When dissolved oxygen levels in water drops below the 5.0 mg/l, aquatic life is put under stress. The lower the DO concentration value, then the greater will be the stress. Oxygen levels that remain below 1-2 mg/l for a few hours can result in large amount fishes kill. According to INWQS, DO value of river water that less than 5 mg/l is classified as Class III and above (Zainudin, 2010).





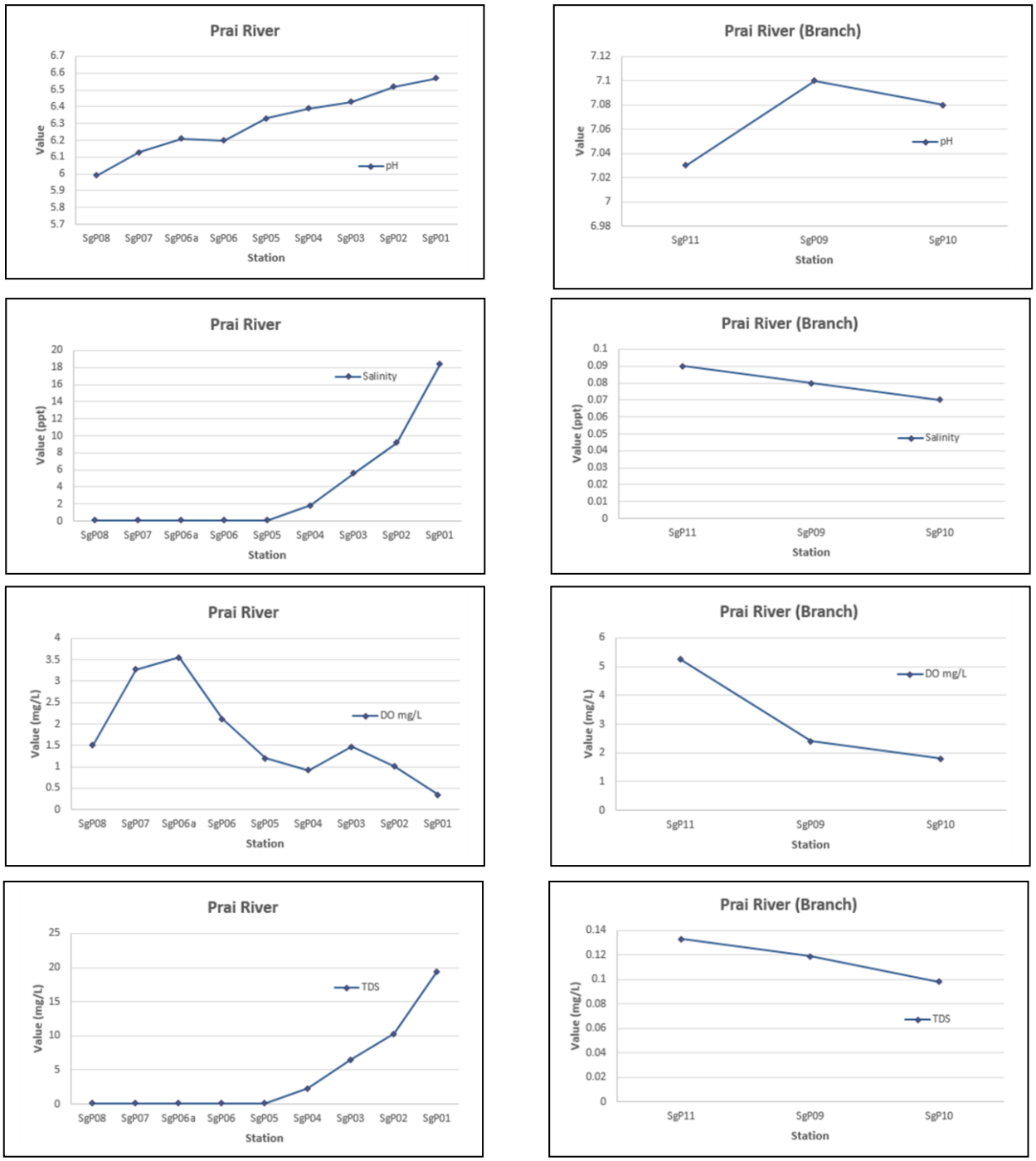


Figure 2: Physical parameters at Perai river and its subsidiary

Particle size analysis

The fraction of clay, silt and sand at various sampling stations were given as in Fig. 3 below. Particle size analyses were performed using small portion (~ 5 g) of the fresh samples. For samples collected at the main Perai river, the percentage of clay, silt and sand were between 15–40 %, 42–78 % and 0–43 %, respectively. Meanwhile, for the subsidiary river, the percentage of clay, silt and sand were between 9–34 %, 39–65 % and 3–53 %, respectively. Most stations found having percentage of silt > clay > sand, except at station SgP 07 and SgP 09 where the sand contains was the highest. Movement of sand might be related to terrestrial erosion due to nearby river activities and also depending on the volume and speed of water flow.

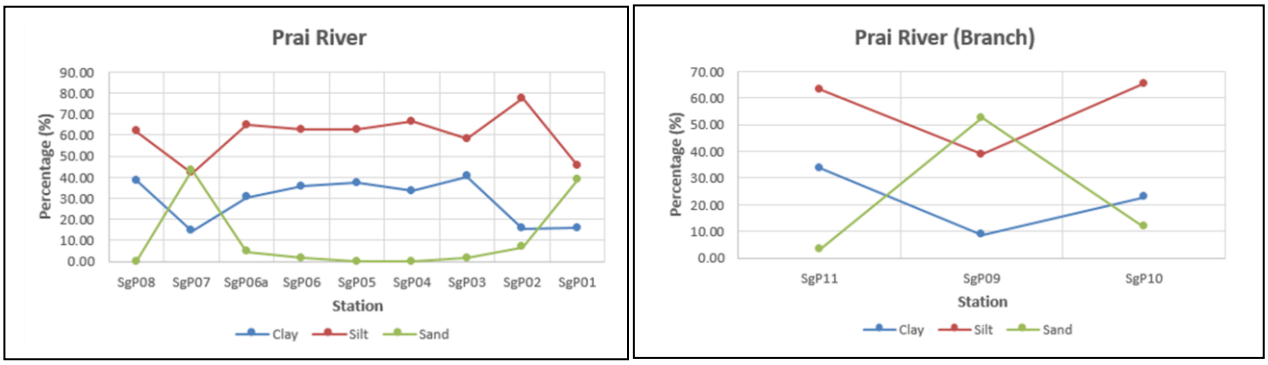


Figure 3: Particle size distribution in sediments at Perai river and its subsidiary

Loss on Ignition

Typically, sedimentary organic matter contains between 40 to 60% of organic carbon. The difference in weight between the 550ºC and 1000ºC ashes may (to first approximation) be assumed as result from loss of carbon dioxide during carbonate mineral break-down. However, loss on ignition techniques cannot indicate which carbonate minerals may be present within any given sample. Because calcium carbonate is (typically) the dominant form of carbonate in most sediments, weight losses at 1000ºC may nonetheless be used to estimate calcium carbonate content. It should be noted that clay minerals may contain significant quantities of lattice-bound hydroxide (as much as five percent by weight) and these ions may be liberated (as water) at high temperatures. Calcium carbonate content estimates from weight losses at 1000ºC may therefore contain errors as great as five percent and (as such) data results are most appropriately reported as losses by weight percent (Nelson & Sommers 1996).

Using equation (1) and equation (2) above, the percentage of organic carbons and the carbonate can be calculated (Fig. 4). The organic carbon for sediments at the Perai river were found varies between 6.3–14.0 % whilst at its subsidiary river were between 5.5–12.5 %. Meanwhile the carbonate contains in sediments were between 2.7–5.2 % and 2.6–4.4 % for the Perai river and its subsidiary river, respectively. Burns et al. (2008) reported that the organic carbon was highest in mixing zone where the processes of flocculation were maximums. Statistical analysis found that significant correlation was observed between the organic matter and the clay content in sediment samples ($r = 0.55$, $p<0.10$) indicating organic matters were mainly bound to the clays fraction in this study area.

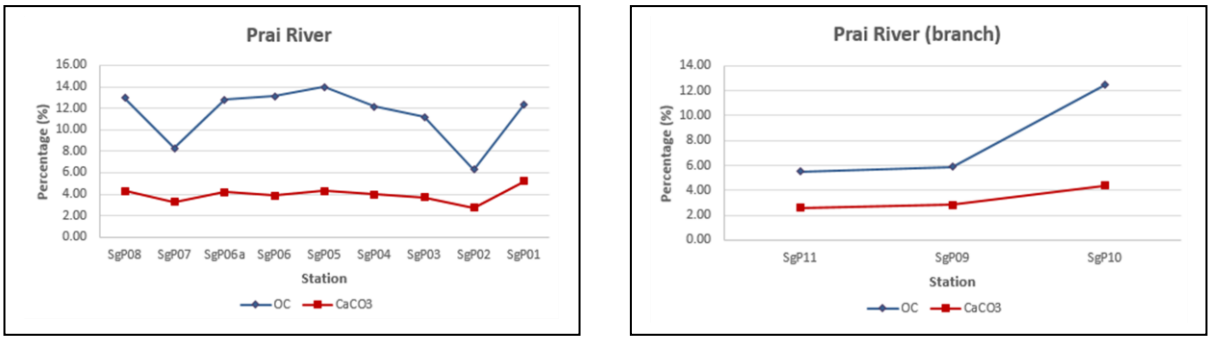


Figure 4: Organic carbon and carbonate distribution in sediments at Perai river and its subsidiary

Elementals analysis

The concentration of elementals in the surface sediments from Perai river were tabulated as in Table 4. Overall, four elements namely Ba, Cr, Fe, Zn were found having maximum concentration values more than 100 ppm whilst As, Sc, Th and U were found having maximum concentration values of more than 10 ppm and the elements Sb and Co were below than 10 ppm. Halves of the elements namely the As, Sb, U, Th and Zn were found to have the mean concentration values greater than the continental crust (CC) values whilst other elements were having lower mean concentrations when compared to the CC values. Among these elements (except of iron), mean concentration for zinc that recorded 244.9 ppm was the highest concentration and it was 4 times higher than the CC value. The greatest difference from the CC values was coming from As where study shown that this element had the mean concentration value ten times greater than the CC value, followed by U (seven folds) and Sb and Th (five times). The mean concentration values for other elements namely Ba, Co, Cr, Fe and Sc found in this study were smaller than the CC values.

Comparison of elemental concentration levels found in sediments in the present study with some previous studies conducted at the Peninsular Malaysia provide better perspectives of the state of metal concentration in the sediment at the study site. First, the concentration of As (9.6–24.8 ppm) found in this study was lower than study by Elias et al. (2018a) (3.6–65.9 ppm, Linggi river) but higher than values reported by Wood et al. (1993) (0.90–12.3 ppm, Juru river) and this study finding was comparable to finding carried out by Lim et al. (2013) (4.5–30.0 ppm, Langat river), Sarmani (1989) (12.4–27.3 ppm, Langat river) and by Sultan et al. (2011) (0.8–23.1 ppm, Terengganu river). The concentration for Ba found ranged from 244 ppm to 501 ppm with an average of 307 ppm. This finding was lower than study conducted by Kamaruzzaman et al. (2002) at Pulau Cik Wan Dagang mangrove forests (231–760 ppm, average 413 ppm) by higher than surface sediment at Juru river by Yii et al. (in press) (235 – 444 ppm, average 297 ppm) whilst element cobalt found in the Perai river surface sediments between 4.6–9.0 ppm was almost double the value reported by Lim et al. (2012) (0.87–4.66 ppm, Langat river).

Meanwhile, from this study, Cr was found in the range of 43.6–130.0 ppm (average 69.8 ppm) which was higher than other studies run by Elias et al. (2018a) at Linggi river (1.7–105.0 ppm), Lim et al. (2013) (4.3–29.0 ppm) at Langat river and Wood et al. (1993) at Juru river (7.0–77.7 ppm) whilst concentration values of Fe (ranged 2.1–3.5 %, average 2.9 %) were much lower than the study performed by Abdus-Salam et al. (2009) at Perak river (20.2–56.6 %) but comparable with studies conducted by Sultan et al.

(2011) at Terengganu river (2.4 %) and by Ahmad et al. (2009) at Kelantan river (3.9 %). On the other hand, Sb concentration found in the surface sediments in this study (0.8–3.3 ppm, average 1.5 ppm) was lower than study reported in surface sediment at Linggi river (0.24–4.44 ppm, average 1.8 ppm) by Elias et al. (2018a). The concentration of Sc found in this study ranged from 7.4 ppm to 12.8 ppm with an average of 11.1 ppm. For elements thorium and uranium, concentration of Th found in surface sediments in this study (23.6–45.9 ppm, average 37.9 ppm) was comparable to study conducted at Juru river by Yii et al. (in press) (24.8–64.0 ppm, average 36.3 ppm) while concentration of U (5.5–17.7 ppm) found in this study was lower than study conducted by Kamaruzzaman et al. (2002) at Pulau Cik Wan Dagang mangrove forests reported values between 11.5–20.1 ppm as well as study by Yii et al. (in press) (5.7 – 22.7 ppm, Juru river).

Elemental Zn had been widely studied by many researchers. The concentration of Zn found in this study ranged from between 97.4–401.0 ppm (average 244.9 ppm). The result was comparable to several studies conducted by Elias et al. (2018a) (12.4–430 ppm, Langat river), Lim & Kiu (1995) (2–483 ppm, Juru river), Sarmini (1989) (71–374 ppm, Langat river) and by Buhari & Ismail (2016) at several different locations (Kuala Juru, Penang, 442.2 ppm; Puluh river, Klang, 256.5 ppm; Minyak Beku, Johore, 241.9 ppm). However, the level of Zn in this study wa higher when compared to those reported by Abdus-Salam et al. (2009) at Perak river (21–160 ppm), Lim et al. (2013) at Langat river (12.3–74.7 ppm), Sultan et al. (2011) at Terengganu river (average 71.3 ppm) and Wood et al. (1993) at Juru river (36.7–83.7 ppm).

Table 4: Concentration of elements (in ppm) for Perai river surface sediment

Element / Station	**As**	**Ba**	**Co**	**Cr**	**Fe**	**Sb**	**Sc**	**Th**	**U**	**Zn**
SgP 08	24.8	264	9.0	130	34300	1.5	12.8	45.9	12.9	238
SgP 07	13.8	284	7.1	43.6	22100	1.0	9.8	38.8	11.2	190
SgP 06a	21.9	292	7.4	65.0	32500	1.4	12.6	44.8	12.7	328
SgP 06	20.0	321	7.4	75.8	34500	1.3	12.4	43.8	11.3	366
SgP 05	22.2	264	7.5	67.8	33800	1.3	12.2	42.1	11.5	401
SgP 04	19.7	283	6.1	60.5	29500	1.3	11.3	39.4	10.4	272
SgP 03	17.7	244	6.6	63.6	31300	0.9	11.7	36.1	9.4	227
SgP 02	9.6	263	5.1	54.9	21000	3.3	7.4	23.6	5.5	164
SgP 01	13.5	280	6.6	61.5	28900	0.8	9.9	36.6	9.5	219
SgP 11	14.0	344	4.6	70.3	22500	1.0	10.2	24.0	6.1	97.4
SgP 09	11.7	501	4.8	69.5	29000	1.8	10.6	33.9	17.7	142
SgP 10	10.9	314	6.0	67.3	27300	1.4	10.9	44.8	16.9	268
Average	**16.9**	**307**	**6.5**	**69.8**	**28900**	**1.5**	**11.1**	**37.9**	**11.4**	**245**
*CC (ppm)	1.7	584	24	126	43200	0.3	16	8.5	1.7	65

*CC = Continental crust values as published by Wedepohl in 1995.

Correlations between the elementals with the iron concentrations, organic matters and particle sizes were summarized and tabulated in Table 5. Six elements were found significantly correlated with the iron concentrations (r = values of 0.80 for As, 0.68 for Co, 0.55 for Cr, 0.89 for Sc, 0.75 for Th, and 0.75 for Zn) and also six elements with the organic matters (r = values of 0.69 for As, 0.78 for Co, 0.79 for Fe, 0.72 for Sc, 0.85 for Th, and 0.87 for Zn). This observation implies that organic matter, is the predominant

carrier of elements to the sediments. Meanwhile, three elements found to have significant correlations (P<0.05) with the clay content were As (r = 0.78), Fe (r = 0.59) and Sc (r = 0.70) suggesting that organic matters carried these three elements were attached to finest particles of clay in the sediments. Antimony and barium were also significantly correlated with silt (r = 0.48, P<0.10) and sand (r= 0.58, P<0.10), respectively. On the other hand, no significant correlations were observed among chromium and uranium with neither the organic matters nor the particle size fractions.

Table 5: Summary of correlation analysis of elemental concentrations with iron, the percentage of organic matter and particle size fractions in surface sediments from Perai river, Malaysia.

Element	Correlation coefficient (r)				
	Iron (Fe)	Organic	Clay	Silt	Sand
As	**0.80[a]**	**0.69[a]**	**0.78[a]**	0.19	**-0.56[b]**
Ba	-0.09	**-0.51[b]**	-0.50	-0.50	**0.58[b]**
Co	**0.68[a]**	**0.78[a]**	0.49	0.01	-0.28
Cr	**0.55[b]**	0.31	0.46	0.14	-0.34
Fe	-	**0.79[a]**	**0.59[a]**	0.01	-0.34
Sb	-0.33	-0.39	-0.35	**0.48[b]**	-0.08
Sc	**0.89[a]**	**0.72[a]**	**0.70[a]**	-0.01	-0.40
Th	**0.75[a]**	**0.85[a]**	0.34	-0.09	-0.14
U	0.42	0.27	-0.21	-0.42	0.37
Zn	**0.75[a]**	**0.87[a]**	0.50	0.27	-0.45

Note: Values in bold are significant at P<0.05 (a) and P<0.10 (b);
"-" value indicate negative correlation.

Enrichment factor

The enrichment factor (EF) is a powerful tool used to elucidate the degree of pollution in sediment with respect to a background value (Lim et al., 2013). Using equation (3) as described earlier, the calculated EF values for the elements of Perai River were given in Table 6. Elements of Ba, Co, Cr and Sc showed no enrichment at all locations. Therefore, all these four elements were believed to be originated predominantly from the lithogenous materials at the study area (Szefer et al., 1996). While looking at elements Sb, Th, U and Zn, generally they were found to be moderately severe enrichment. Only one station having Sb concentration (station SgP 02), and three stations having U concentrations (stations SgP07, SgP 09 and SgP 10), which were considered as severely enriched. Meanwhile, two stations with Sb contents, and four stations with Zn contents were found only having moderate enrichment in the sediments. Finally, arsenic elements were found to be severely enriched at all stations along the river. EFs of elementals can be valuable and have been used as an indirect indicator for evaluation of sediment contamination or toxicity. However, using enrichment factor alone is not sufficient for evaluation of sediment toxicity at a particular site. Consideration for the degree of contamination in sediment and comparison with sediment guidelines are more useful approach to evaluate toxicity of the sediment for the particular site (Elias et al., 2018a). This information will discuss elsewhere.

From this study, several elements namely the As, Sb, U, Th and Zn showed high degree of enrichments. The study area is densely populated and comprises of lots of heavy industrials; therefore the most probable sources of pollution might be coming from the manufacturing industries, agriculture and sewage

emission (Shazili et al., 2006). The use of arsenical herbicides in plantations along the river could be a source of arsenic pollution (Sarmani, 1989). Meanwhile, antimony could enters the environment during the mining and processing of antimony-containing ores (such as stibnite, sibiconite, tetrahedrite, ullmannite) and in the production of antimony metals, alloys and antimony oxide, and combinations of antimony with other substances. Antimony is usually mixed with other metals such as lead and zinc to form mixtures of alloys. Antimony alloys are used in lead storage batteries, solder, sheet and pipe metal, bearings, castings, type metal, ammunition and pewter. Antimony trioxide is used in the production of polyethylene terephthalate (PET) water bottles (ATSDR, 2008). On the other hand, Th and U found in the sediments most likely coming from the terrestrial sources of natural radioactivities (NORM) of Th-series and U-Series and soil run-off. Human activities such as usage of artificial phosphate fertilizers in agricultural production as well as from the nearby factories processing NORMs materials such as concretes, cements, plasters, quarries, etc could also contributed to this. Finally, zinc foils roofing which were widely used for houses and restaurants along the rivers were believed to be contributing to the high zinc contents in the river.

Table 6: Enrichment factor (EF) of elementals for Perai river surface sediment

Element / Station	**As**	**Ba**	**Co**	**Cr**	**Sb**	**Sc**	**Th**	**U**	**Zn**
SgP 08	**18.4**	0.6	0.5	1.3	**6.3**	1.0	**6.8**	**9.6**	**4.6**
SgP 07	**15.9**	1.0	0.6	0.7	**6.5**	1.2	**8.9**	**12.9**	**5.7**
SgP 06a	**17.1**	0.7	0.4	0.7	**6.2**	1.0	**7.0**	**9.9**	**6.7**
SgP 06	**14.7**	0.7	0.4	0.8	**5.4**	1.0	**6.5**	**8.3**	**7.1**
SgP 05	**16.7**	0.6	0.4	0.7	**5.5**	1.0	**6.3**	**8.6**	**7.9**
SgP 04	**17.0**	0.7	0.4	0.7	**6.3**	1.0	**6.8**	**9.0**	**6.1**
SgP 03	**14.4**	0.6	0.4	0.7	**4.1**	1.0	**5.9**	**7.6**	**4.8**
SgP 02	**11.6**	0.9	0.4	0.9	**22.6**	1.0	**5.7**	**6.7**	**5.2**
SgP 01	**11.9**	0.7	0.4	0.7	**4.0**	0.9	**6.4**	**8.4**	**5.0**
SgP 11	**15.8**	1.1	0.4	1.1	**6.4**	1.2	**5.4**	**6.9**	**2.9**
SgP 09	**10.3**	1.3	0.3	0.8	**8.9**	1.0	**5.9**	**15.5**	**3.3**
SgP 10	**10.1**	0.9	0.4	0.8	**7.4**	1.1	**8.3**	**15.7**	**6.5**
Average	**14.7**	0.8	0.4	0.8	**7.8**	1.0	**6.7**	**10.1**	**5.5**

* Values in bold indicate enrichment.

CONCLUSIONS

Neutron Activation Analysis (NAA) technique was used to quantify the concentration levels of several elements (As, Ba, Co, Cr, Fe, Sb, Sc, U, Th, and Zn) in the surface sediments collected at Perai River, Penang. Halves of the studied elements namely the As, Sb, U, Th and Zn were found having the mean concentration values that were greater than the continental crust (CC) values whilst other elements were found having lower mean concentrations as compared to CC values. Six of the elements were found significantly correlated with the iron concentrations and also with the organic matters but no clear correlations were observed among elements with the particle size fractions. By using the iron (Fe) as the normalization element, As was the only element found to be severely enriched among all the elements. Sb, Th, U and Zn were found to be moderately severe enriched while Ba, Co, Cr and Sc showed no

evidence of enrichment and believed to be originated predominantly from the lithogenous materials at the study area. Human development activities such as industries and urbanization were believed to be the main contribution to the enrichment of elements.

ACKNOWLEDGEMENTS

The authors would like to express their special appreciations to the International Atomic Energy Agency for providing research funding under research grant, K41016–RC 20884. We would also like to thank the personnel of Radiochemistry and Environment Group (RAS), Analytical Chemistry Group (ACA) and Material Technology Group (MTEG) for their support and cooperation throughout this study.

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