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Heavy Metals Concentration in Surficial Sediments of Bidong Island, South China Sea off the East Coast of Peninsular Malaysia

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ABSTRACT

The distribution, enrichment and accumulation of heavy metals in the surficial sediments of Bidong Island, South China Sea East Coast of peninsular Malaysia were investigated. Thirty sediment samples were collected in 2007 using Smith McIntyre grab and characterized for heavy metal content. Results showed that the average concentration of heavy metals were Cu (19.33±5.78 μg g^{-1} dry weight), Zn (61.34±9.36 μg g^{-1} dry weight), Cd (0.15±0.06 μg g^{-1} dry weight), Pb (20.47±5.36 μg g^{-1} dry weight), Cr (47.04±16.05 μg g^{-1} dry weight), Al (6.23±2.33 μg g^{-1} dry weight) and Fe (4.21±1.41 μg g^{-1} dry weight), respectively. All metals studied have relatively low Enrichment Factor (EF) values and index of geo-accumulation (I_{geo}) in the study area. Overall, the geochemistry of the sediment of Bidong Island was influenced by both natural and anthropogenic inputs to the catchment. However, direct comparison with earth crust values and normalization to Al indicated that natural processes were more dominant than anthropogenic inputs in concentrating metals.

Key words: Enrichment, accumulation, enrichment factor, index of geoaccumulation, anthropogenic

INTRODUCTION

Pollution by heavy metals in natural environments has become a global problem (Irabien and Velasco, 1999). It has been recognized for many years that the concentrations of metals found in coastal areas, whether they are in the dissolved or particulate phase may be derived from a variety of anthropogenic and natural sources (Burridge *et al*., 1999). Heavy metals are of considerable environmental concern due to their toxicity, wide range of sources, nonbiodegradable properties and accumulative behaviors. With the rapid industrialization and economic development in coastal regions, heavy metals are continuing to be introduced to estuarine and coastal environment through rivers, runoff and land-based point sources where metals are produced as a result of metal refinishing by-products. In most circumstances, the major part of the anthropogenic metal load in the sea and sea bed sediments and organisms has a terrestrial source from mining and intensive aquaculture and municipal wastewaters, untreated effluents, harbor activities, urban and agricultural runoff along major rivers and estuaries and bays (Dalman *et al*., 2006).

When metals enter the marine environment, most of them will settle down and be incorporated into sediments together with organic matter, Fe/Mn oxides, sulfides and clay (Wang and Chen, 2000). Marine sediments act as scavengers for trace metals and often provide an excellent proof of man's impact (Guevara *et al*., 2005). To some extent, trace metal contents in sediment can reflect the quality of the water body. Although sediments act as one of the ultimate sinks for heavy metals input into the aquatic environment, they cannot fix metals permanently. Some of the sediment bound metals might be released into the water body again through various processes of remobilization under variable conditions. Moreover, marine organisms or biota can accumulate metals, which thus enhances the potential of some metals entering into the food chain (Yu *et al*., 2008).

Contamination in coastal sediments by heavy metals has been a problem since these environments often receive heavy metal wastes generated naturally through the weathering of rocks and through a variety of human activities (Gomez-Parra *et al*., 2000). In coastal environments, heavy metals discharged from sources such as industrial and sewage effluents may accumulate in bottom sediment as the suspended particles on which they are adsorbed settle out (Huh *et al*., 1992). Consequently, heavy metal concentrations in sediments near large population centers are often significantly higher than those in the sediments that have little history of contamination (Hornberger *et al*., 1999). When elevated, heavy metals can exert toxic effects, including those that are biologically essential. Understanding of ecological and environmental consequences of heavy metals in coastal sediments is a complex problem, but one that must be thoroughly investigated to make good decisions for protecting exposed aquatic habitats.

Bidong Island is an unpopulated Island about 8 nm off the coast off Terengganu. However from 1975-1990, the Island was a UNHCR refugee camp for a quarter of a million Vietnamese "Boat people" escaping the Vietnam War. Due to its history the Terengganu State government plans to develop Bidong Island as a heritage tourism site and a new scuba diving destination. This study was thus carried out to determine baseline metal concentrations in the sediment as a reference for future studies.

MATERIALS AND METHODS

The South China Sea is a unique area, located between the Pacific Ocean and the Asian Continent. As a semi-enclosed basin in connection with the open ocean, it is able to record both global (glacial/interglacial oscillations) and local (monsoon) climatic changes. This marginal sea is fed by three of the biggest rivers in the world, in term of sediment load, Mekong River (160×10^6 t y^{-1}), Red River (130×10^6 t y^{-1}) and Pearl River (100×10^6 t y^{-1}), respectively (Boulay *et al*., 2005). Sediment input from these rivers have been shown to provide reliable data about the paleo environmental variations affecting the Southeast Asian continent (Wang *et al*., 1999; Wehausen and Brumsack, 2002; Kissel *et al*., 2003; Liu *et al*., 2003).

Bidong Island is situated about 8 nm from the mainland of Terengganu and has a shallow environment, with water depth of up to 15 m. The sediment is composed of sandy mud with coral debris and shell and part of the sediment is derived from the Terengganu River some 14 nm to the South of the Island and the Merang River across the Island.

Sediment samples were collected from 6 transects (30 sampling stations) surrounding Bidong Island (Fig. 1) with a Smith McIntyre grab to obtain surface sediment. This oceanographic fieldwork was accomplished with the UNIPERTAMA VII research vessel from University Malaysia Terengganu. During sampling, precautions were taken to minimize any disturbance in the grain-size distribution of the original sediment. Samples were taken only when the grab was firmly closed on arrival on the boat deck, so as to avoid any leaks of fine material withdrawn by water. In addition, to avoid metal contamination from the grab's wall, the outermost layer of the sediment sample was removed and only the inner part was kept. After collection the samples were placed in plastic containers and kept at 4°C until analysis (Azrina *et al*., 2006).

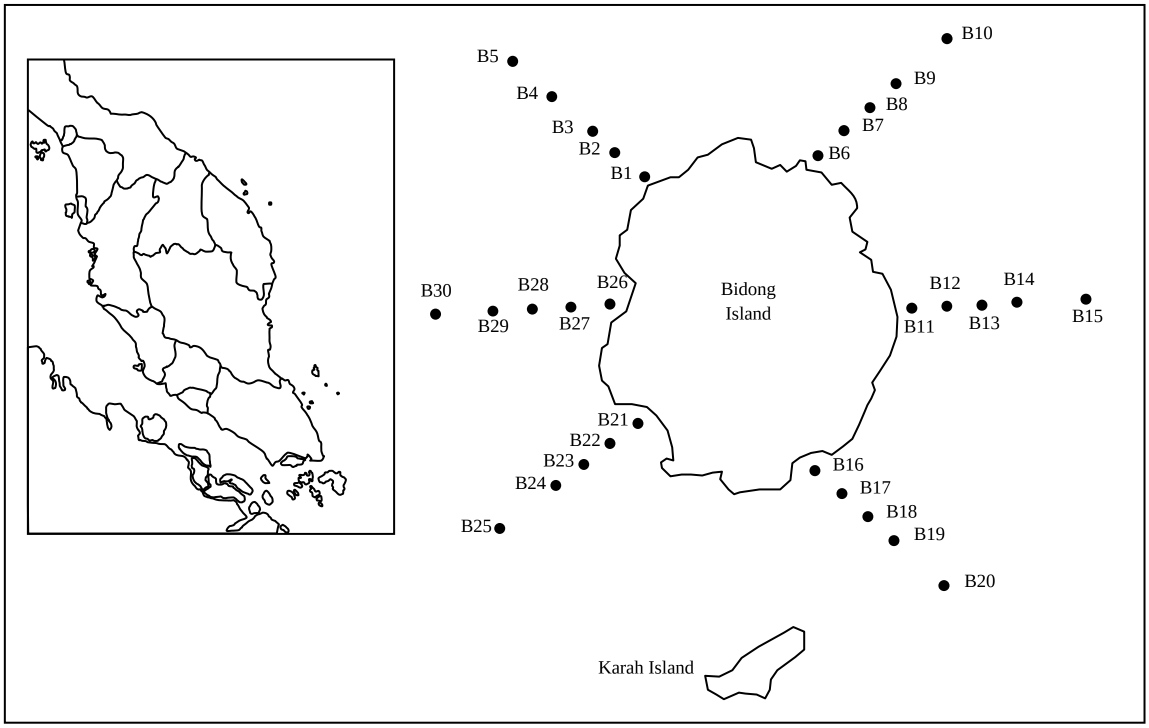

Fig. 1: Map showing sampling location off the Bidong Island, Terangganu

The sediment samples were digested and the analyses for total Pb and Cu carried out following published methodologies with some modifications (Gupta and Bertrand, 1995; Yap *et al*., 2002; Defew *et al*., 2005). An inductively coupled plasma mass spectrometer (Perkin Elmer Elan 6000 ICP-MS) was used for the quick and precise determination of Co, Cu, Pb and Zn in the digested sediment. The digestion method involved heating of 50 mg of a finely powdered sample in a sealed Teflon vessel in a mixture of acid solution (1.5 mL) of concentrated HF, HNO_3 and HCl. The Teflon vessel was kept at 150°C for 5 h. After cooling, a mixed solution of boric acid and EDTA (3 mL) was added and the vessel was again heated at 150°C for 5 h. After cooling at room temperature, the content of the vessel was transferred into a 10 mL polypropylene test tube and was diluted to 10 mL with deionized water. A clear solution with no residue was obtained at the last stage. The precision assessed by the replicate analyses was less than 3%. The accuracy was also examined by analyzing duplicate Canadian Certified Reference Material Project MESS-3, the results of which were within ±3% of certified values.

RESULTS AND DISCUSSION

Figure 2 shows the concentration of Cu, Zn, Cd, Pb, Cr and Fe (in $\mu g\ g^{-1}$ dry wt.) in surface sediment of Bidong Island. The average concentration of Cu was 19.39±5.78 $\mu g\ g^{-1}$ with a range of 10.69-32.77 $\mu g\ g^{-1}$. Generally, the Southern part of Bidong Island had the highest concentrations of Cu compared to northern part. The concentrations are lower than global average shales of 55 $\mu g\ g^{-1}$ Cu (Taylor, 1964). In contrast, Zn concentrations were generally lower at the Southern part compared to Northern part. The Zn concentration ranged from 47.58-88.00 $\mu g\ g^{-1}$, with an average concentration of 61.34±9.36 $\mu g\ g^{-1}$. This value is comparable to average shale of 70 $\mu g\ g^{-1}$ dry weights (Taylor, 1964). Meanwhile for Cd, the concentration was well distributed in

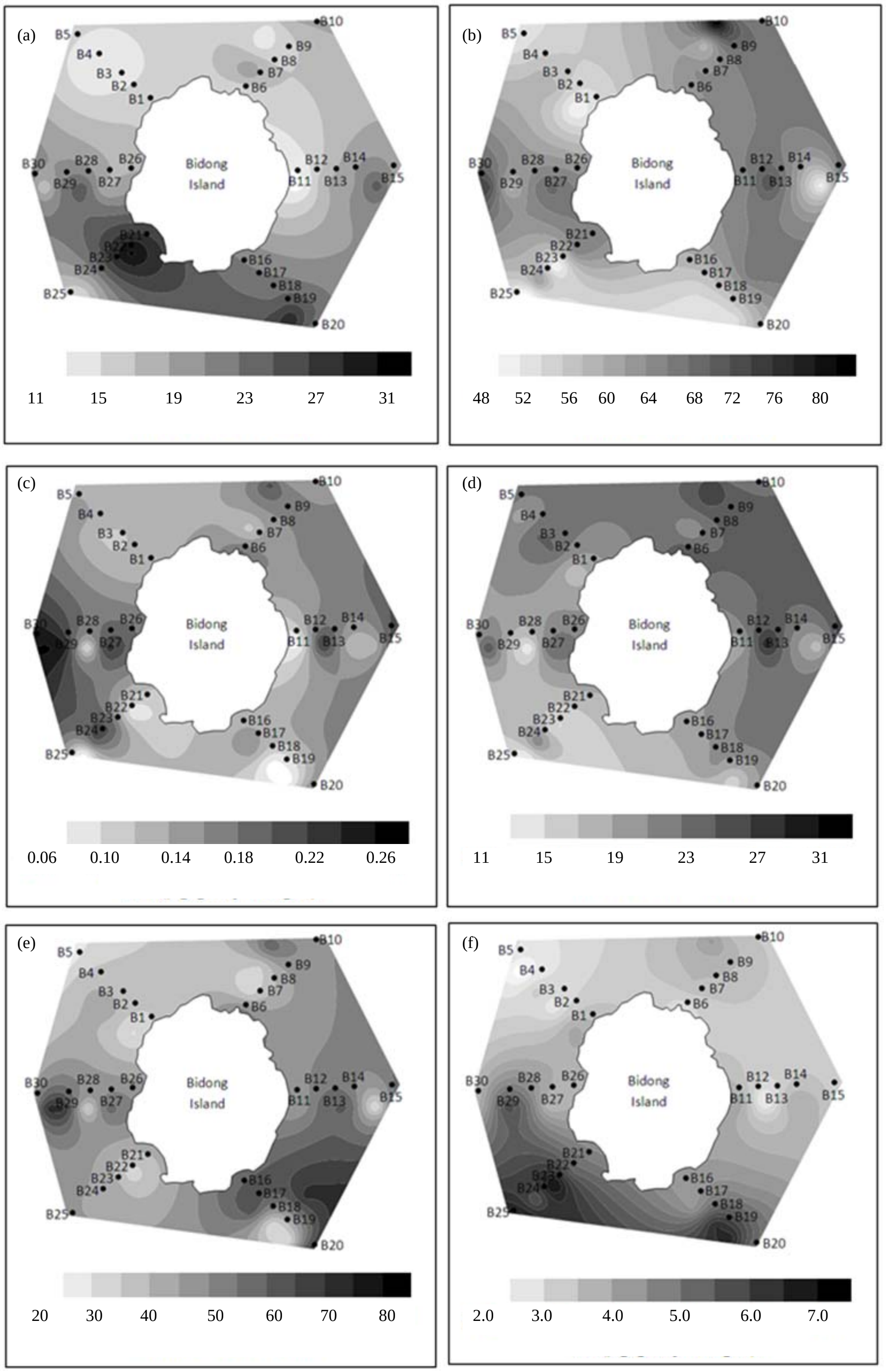

Fig. 2(a-f): Concentration isopleth maps for metal distribution in Bidong Island surface sediment, (a) Cu, (b) Zn, (c) Cd, (d) Pb, (e) Cr and (f) Fe (µg g^{-1} dry weight) the sediment surrounding Bidong Island. The average value, 0.16±0.06 μg g^{-1} and range of concentration of 0.05-0.27 μg g^{-1} was lower compared to the average shale (Taylor, 1964) Cd concentration of 0.2 μg g^{-1}.

For Pb, the northern part of the Island had the higher concentrations compared to the southern part. The average concentration of Pb was 20.47±5.36 μg g^{-1}, with a range of 11.15-32.13 μg g^{-1}. These values are generally higher than the average shale concentration of 13 μg g^{-1} dry (Taylor, 1964). For Cr, the Western and the Eastern side of Bidong Island had the higher levels of the metal. The average concentration, 47.04±16.05 μg g^{-1} was two times lower compared to the average shale (Taylor, 1964) concentration of 100 μg g^{-1}. Cr concentration ranged from 20.74-77.88 μg g^{-1}. Similar with Cu, the Fe concentration was also high in the southern part of Bidong Island. The concentration ranged from 1.98-7.12%, with an average value of 4.21±1.41% which is comparable to average shale concentration of 5% (Taylor, 1964).

Anthropogenic activities had caused important transformation in coastal environments during the last 150 years. Heavy metals were among the most widespread of the various pollutants originating from anthropogenic activities, particularly from mining and smelting waste sites (Mendil and Uluozlu, 2007; Adamo *et al*., 2005). The approach most often used to determine the sources of the pollutant is through the normalization of geochemical data to a reference metal. The reference metal must therefore be an important constituent of one or more of the major fine-grained trace metal carriers reflect their granular variability in the sediment. The most often used reference metal is Al, which represents a chemical tracer of Al-silicates, particularly the clay minerals (Van der Weijden, 2002; Liaghati *et al*., 2004; Daessle *et al*., 2004). For a better estimation of anthropogenic input, an enrichment factor was calculated for each metal by dividing its ratio to the normalizing element by the same ratio found in the chosen baseline. Enrichment Factor (EF) values are applied to evaluate the dominant source of the sediments and as indicators for pollution (Hung and Hsu, 2004; Mil-Homens *et al*., 2007) and described as EF = $(E/Al)_{sed}/(E/Al)_{crust}$ where $(E/Al)_{sed}/(E/Al)_{crust}$ are the relative concentrations of the respective element E and Al in the sediment and in the crustal material, respectively (Prudencioa *et al*., 2007; Zhang *et al*., 2007). Enrichment Factor (EF) values close to 1 point to a crustal origin, while those with a factor more than 10 are considered to have a non-crustal source. In this study, the elements studied were proven to be deficient to minimal enrichment, with EF values in the range of 0.20-1.45 (Cu), 0.56-3.65 (Zn), 0.25-3.31 (Cd), 0.86-6.95 (Pb), 0.22-1.55 (Cr) and 0.62-3.96 (Fe) (Table 1 and Fig. 3).

In order to compare the status of heavy metal concentrations with the background values, index of geoaccumulation (I_{geo}) was computed. Geoaccumulation (I_{geo}) describes the relationship between the measured element concentration in the sediment fraction (Cn) and the geochemical value in fossil argillaceous sediment (average shale), Bn. The constant value, 1.5 allows natural fluctuations in the content of a given substance in the environment and has very small anthropogenic influences (Chatterjee *et al*., 2007; Audry *et al*., 2004).

Table 1: Enrichment factors for metals in Bidong Island surface sediment

Elements	EF Values	Sources
Cu	0.52±0.25	Deficiency to minimal enrichment
Zn	1.38±0.75	Deficiency to minimal enrichment
Cd	1.26±0.74	Deficiency to minimal enrichment
Pb	2.58±1.71	Deficiency to minimal enrichment
Cr	0.72±0.37	Deficiency to minimal enrichment
Fe	1.27±0.71	Deficiency to minimal enrichment

Table 2: I_{geo} value for metals in Bidong Island surface sediment

Elements	I_{geo}	Sources
Fe	0.69±0.17	Uncontaminated to moderately contaminated
Cr	0.76±0.07	Uncontaminated to moderately contaminated
Cu	0.66±0.07	Uncontaminated to moderately contaminated
Zn	0.88±0.03	Uncontaminated to moderately contaminated
Cd	1.61±0.38	Moderately contaminated
Pb	1.00±0.09	Moderately contaminated

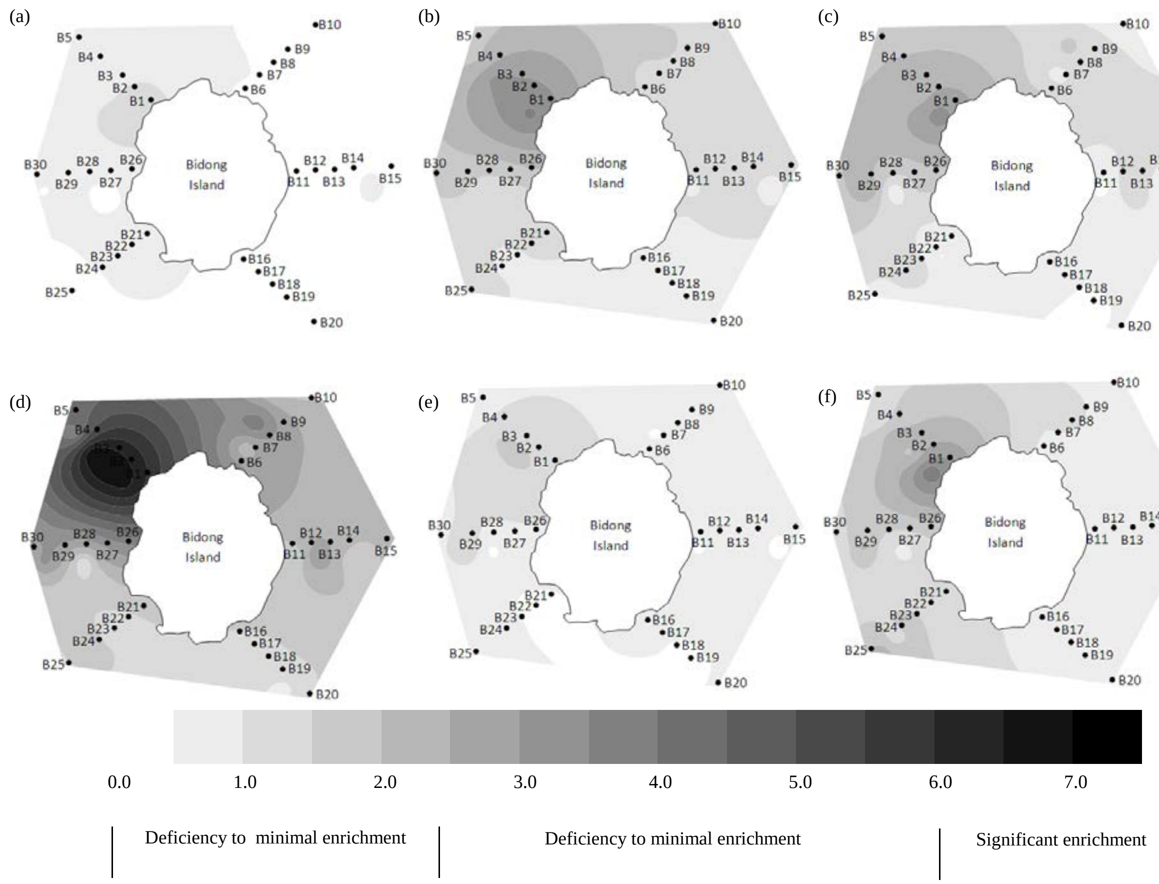

Fig. 3(a-f): Isopleth maps for enrichment factor values in surface sediment off Bidong Island, (a) Cu, (b) Zn, (c) Cd, (d) Pb, (e) Cr and (f) Fe

$$I_{geo} = \log_2 (Cn/1.5B_n)$$

In this study, all elements have calculated (I_{geo}) values less than 1.0 except Cd (1.61) and therefore can be classified as practically uncontaminated to moderately contaminated (Table 2). Based on the EF and (I_{geo}) values, it can be suggested that the sources of heavy metals in the Bidong Island environment is solely natural, coming from the Terengganu River as one of the main sources and from other rivers to the South and the Merang River closest to the Island. The relative metal deficiency measured in the Bidong Island sediment may be due to dilution of the metals by sand as well as coral and shell material abundant in the coastal environment of the Terengganu coast (Fig. 4).

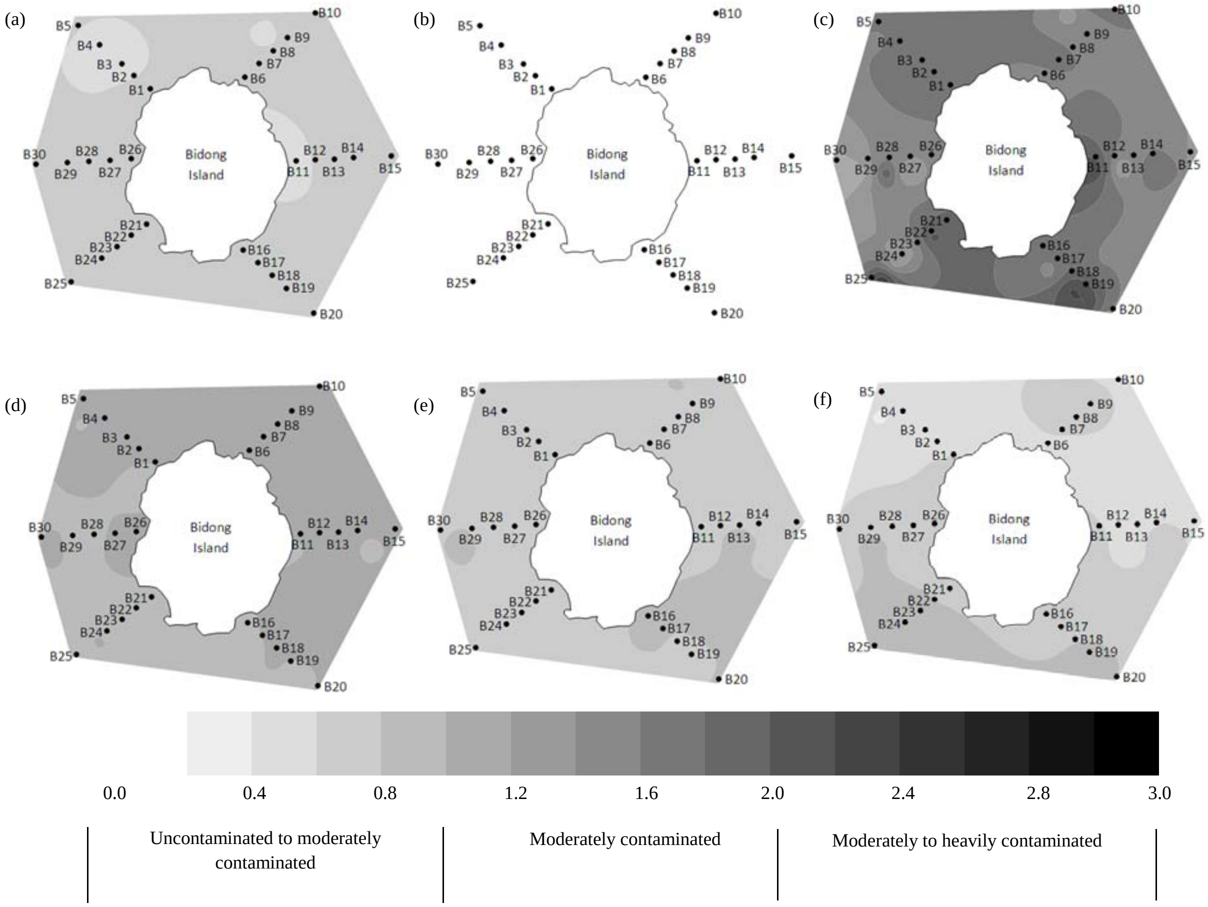

Fig. 4(a-f): Isopleth maps for I_{geo} values in surface sediment off Bidong Island, (a) Cu, (b) Zn, (c) Cd, (d) Pb, (e) Cr and (f) Fe

CONCLUSION

Generally metal concentrations in the sediment of Bidong Island is mainly influenced by natural processes. The EF and I_{geo} values indicates that the metals studied occurred in both lithogenous and non-lithogenous fractions. In brief, it can be concluded that there was minimal anthropogenic influence of heavy metals in surface sediment surrounding Bidong Island of Terengganu. The results would be useful as a baseline for comparison of future monitoring studies of sediment quality.

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