Sains Malaysiana 48(1)(2019): 45–59
http://dx.doi.org/10.17576/jsm-2019-4801-06

Determination of the Sediment Contamination Level in Dangli Waters of Langkawi UNESCO Global Geopark, Kedah, Malaysia

(Pengenalpastian Tahap Pelumusan Sedimen di Perairan Dangli di Langkawi UNESCO Global Geopark, Kedah, Malaysia)

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ABSTRACT

Dangli Waters ecosystem is located at the north of Langkawi UNESCO Global Geopark. Apparently, this area is currently experiencing a significant deterioration of marine habitat. Therefore, 14 stations were set up in this study area to investigate the sediment for metal contents discharged into Dangli Waters using the ecological risk assessment. The sediment samples were collected during four seasons, namely South West Monsoon, First Inter Monsoon, North East Monsoon and Second Inter Monsoon. The spatial distribution pattern of heavy metals in sediment was properly determined as well as the seasonal variation of the contamination. From the results obtained, the average concentration of each heavy metal distributed in the surface sediment of Dangli Waters can be written in decreasing order as Fe>Cr>As>Co>Cd. From the observation, heavy metal concentrations of As was recorded the most higher profiles near to the cement plant production area. Meanwhile, for the pattern of seasonal changes, FIM season was defined as the season with higher concentrations of all metals in the surface sediment compared to other seasons. This is due to highly rainfall distribution and water runoff during this period, leading an increase of sediment deposition into the Dangli Waters. According to the contamination factor (C_f) for each metal, it was shown that some heavy metals such as As were at a risky level with the C_f value was higher than 6 (C_f >6). However, the degree of contamination (C_d) for each station was classified as moderate ($7 \leq C_d < 14$), except for ST2 which showed a low degree of contamination.

Keywords: Contamination degree (C_d); *contamination factor* (C_f); *heavy metal; sediment*

ABSTRAK

Ekosistem Perairan Dangli terletak di utara Langkawi UNESCO Geopark. Jelas sekali, kawasan ini sedang mengalami kemerosotan habitat marin yang amat ketara. Oleh yang demikian, 14 stesen kajian telah diwujudkan di perairan ini bagi mengkaji dan mengenal pasti taburan kepekatan logam berat yang dilepaskan ke Perairan Dangli dengan menggunakan penilaian risiko ekologi. Persampelan sedimen permukaan laut dijalankan ketika musim Monsun Barat Daya, Peralihan Monsun Pertama, Monsun Timur Laut dan Peralihan Monsun Kedua. Secara amnya, corak sebaran dan taburan logam berat dalam sedimen serta variasi bermusim ke atas kontaminasi telah diteliti dengan sempurna pada sepanjang tempoh kajian ini dijalankan. Daripada keputusan yang diperoleh, purata taburan kepekatan setiap logam berat di dalam sedimen permukaan Perairan Dangli boleh dinyatakan dalam urutan menurun iaitu Fe> Cr> As> Co> Cd. Daripada pemerhatian, kepekatan logam berat bagi As mencatat profil kepekatan yang paling tinggi berhampiran dengan kawasan kilang pengeluaran simen. Manakala bagi corak perubahan musim pula, FIM ditafsirkan sebagai musim yang mempunyai purata kepekatan yang lebih tinggi bagi semua logam berbanding musim-musim yang lain. Ini adalah disebabkan oleh taburan hujan dan aliran air daratan yang sangat tinggi pada tempoh ini yang membawa kepada peningkatan pemendapan sedimen ke dalam Perairan Dangli. Menurut faktor pencemaran (C_f) bagi setiap logam, ia menunjukkan bahawa sesetengah logam berat seperti As berada pada tahap berisiko tinggi dengan kadar nilai C_f adalah lebih tinggi daripada nilai 6 (C_f > 6). Walau bagaimanapun, tahap pencemaran (C_d) bagi setiap stesen telah dikelaskan sebagai sederhana ($7 \leq C_d < 14$), kecuali ST2 yang menunjukkan tahap pencemaran yang rendah.

Kata kunci: Darjah pencemaran (C_d); faktor pencemaran (C_f); logam berat; sedimen

INTRODUCTION

Nowadays, most of the pressure experienced by the marine ecosystem is attributed to land-based pollution, particularly the inflow of toxicant substances, sediment, and nutrients into the marine ecosystem. The impacts from the land-based pollution consisting of coastal development, deforestation, agricultural runoff, oil and chemical spills, refinery production and failures of septic system and solids waste management will cause disruptions in ecological functions, inhibit growth and reproduction, and spread diseases as well as mortality among sensitive species (Al-Rousan et al. 2007; Chinnaraja et al. 2011; Duruibe et al. 2007; Mazlan et al. 2005; Waddell 2002).

Previous studies have been carried out extensively in the marine environment to determine the concentration of heavy metals in marine organisms and their ecosystem

itself. According to Idris et al. (2007), heavy metals referred to as lethal metals (Hg, As, and Cd) are toxic to aquatic biota and humans at low concentrations. However, some heavy metals (Cu, Fe, Zn) are essential to the aquatic organisms for their proper physiological and biochemical functions at the trace level (Mohdzahir et al. 2012). The consequences of the anthropogenic inclusion into this fragile ecosystem will lead non-targeted organisms such as fish, marine invertebrates and plankton to harm. Apart from that, coral reefs are the most sensitive of all the entire ecosystems to pollution, climate change and diseases. Jitkue et al. (2007) stated that these ecosystems are very sensitive to natural and anthropogenic pressures.

Langkawi Archipelago is a good example to be studied (Figure 1). Generally, this archipelago consists of 99 islands with an area of about 47,848 ha (Shamshiry et al. 2011). The tourism industry has been growing aggressively since the declaration of a duty-free island in the year 1987, thus became the main source for the island's economy. Quite recently, in the year 2015, this archipelago has been upgraded from Langkawi Geopark, to Langkawi UNESCO Global Geopark (LUGG). Consequently, sustainable developments of coastline areas need to be strengthened to ensure the sustainability of marine life in these islands to be unaffected. In general, most of the coral colonies in this island are living in stressful conditions. According to Hendry and McWilliams (2001), most of coral colonies at the northern coast of LUGG were experiencing serious deterioration. If sustainable development is not applied, the sustainability of corals around this island will become threatened and destroyed, thus contributing to the collapse of the marine ecosystem.

Therefore, to empower the Geopark area, an assessment of heavy metal contamination in the surface sediment of Northern Coast of Langkawi UNESCO Global Geopark has been carried out. The outcome of this ecological risk assessment is particularly important in aiding the process of determining corrective measures and necessary actions that are to be made and enforced by the local authorities, so that the coral reef environment can be maintained and sustained. Apart from that, this assessment will also provide basis information for assessments of the impact of heavy metal pollution on the marine environment especially coral reefs and ultimately help the management of LUGG sustain resilience of coral reefs for future generations.

Materials and Methods

Study Area

Dangli Waters consist of three small islands namely Dangli, Pasir and Gasing islands. These islands are located at the northern part of Langkawi Island, in which the estimated size of each island is of 0.06, 0.03 and 0.05 km^2, respectively. This uninhabited island is clearly visible from the Tanjung Rhu beach. Looking at the geological structure, these islands have rocky surfaces with only 40% of them covered in tropical forest. It is not a wonder that it became one of the icons of Langkawi UNESCO Global Geopark.

From the observation, there was a petroleum depot and cement plant still operating near to Teluk Ewa area. This is likely to be considered as one point-source pollution for this area. Moreover, according to Figure 1, there are two major estuaries existing in this area, located at the southwest (Kuala Kubang Badak) and east (Kuala Ayer Hangat) of the island. According to 15 years of average rainfall distribution data (2000-2015) from the Department of Meteorology Malaysia, heavy rainfalls were recorded during FIM season (Sept-Nov) with 302.20 mm, followed by SWM (June-Aug) and SIM (Mar-Apr) seasons with 292.40 mm and 187.00 mm, correspondingly. However, comparatively, the driest

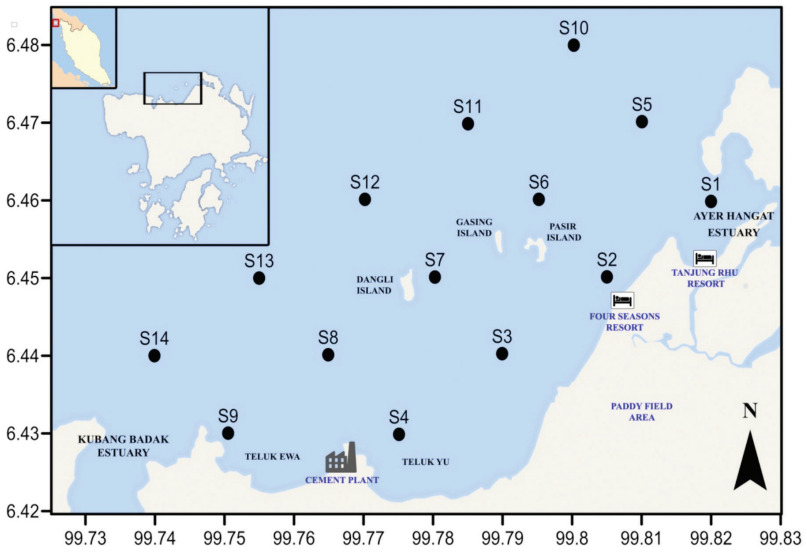

FIGURE 1. Study area

months seemed to have started in December and lasted until February (NEM) with a much less rainfall distribution (47.4 mm) throughout the year.

SAMPLE COLLECTION AND PRESERVATION

Sample collection activity was conducted during four seasons, namely South-West Monsoon (SWM), First Inter-Monsoon (FIM), North-East Monsoon (NEM) and Second Inter-Monsoon (SIM). Fourteen stations were established along the Northern Coast of Dangli Waters and marked using the Global Positioning System (Table 1). These locations were selected based on the fact that they might have been impacted by the nearby source of contamination (i.e. cement plant, petroleum depot, resort, agriculture activity, port, and golf course). Sediment samples from the seabed surface were collected using the Van Veen Grab, where afterwards, samples were placed in plastic bags that were previously immersed in 5% nitric acid for two to three days to prevent sample contamination. The sediment samples were then preserved in the ice-box at 4°C in order to maintain the original condition of samples. At the laboratory, samples were then dried in the oven at 105°C for 24 h. For heavy-metal analysis, it was ensured that the samples have been completely dried prior to grinding using a mortar and pestle, and later sieved under 63 µm. Precautions in preventing sample contamination were given priority. Samples were then stored in labelled plastic vials and kept in the drying cabinet awaiting further lab analysis.

SAMPLE DIGESTION

In this study, the digestion and analytical procedures were adopted and applied from that of Tsunogai and Yamada (1979), Kamaruzzaman (1999) and Jamil (2006) with little modifications. For this analysis, 0.05 g of the fine powder sediment (<63 µm) was weighed and put into a Teflon vessel. After that, 1.5 mL of mixed acid (2.5 HF: 3 HNO3: 3 HCL) was added into the Teflon vessels using a single channel pipette, 100-1000 micro litre (µL) of the brand CappAero which was ISO 9001; 2000 certified. This digestion method is also known as the aqua regia + HF digestion method, which was also applied by Trimm et al. (1998) and Chen and Ma (2001). Finally, the Teflon Bomb jackets were screwed tightly to prevent the appearance of silicate gel on their bodies, before placing the Teflon Bombs into the oven for 6 h at 160˚C. After 6 h, they were cooled down under room temperature where after that, 3.0 mL of acid solution composed of Ethylenediaminetetraacetic acid (EDTA) and Boric acid was added. The samples were then again put into the oven at 160˚C for another 6 h. The clear solution obtained was then transferred into centrifuge tubes and meshed-up to 10 mL with Mili-Q water.

To verify the precision of the analytical procedures, the sediment samples were analysed in three replicates for each sampling point, including a blank sample. While to confirm analytical accuracy, portions of certified reference materials (SRM1646a - estuarine sediments) from the National Institute of Standards and Technology (NIST) were analysed with each batch of samples. The concentrations of metals (As, Cd, Co, Cr and Fe) in the final digested solutions were then measured using the Inductively Coupled Plasma Mass Spectrometer (Perkin Elmer. Elan 9000). The recovery rates of the heavy metals in the SRM1646a are listed in Table 3.

EVALUATION OF SEDIMENT POLLUTION

The contamination factor (C_f) and the degree of contamination (C_d) were widely used to evaluate the level of sediment contamination (Dehghan Madiseh et al. 2009; Hakanson 1980; Muller 1969; Tomlinson et al. 1980). The C_f and C_d are calculated as follows;

$$C_f = C_e/C_b$$

TABLE 1. The coordinates of each sampling station

STATION	LONGITUDE	LATITUDE
ST1	99.81998°E	6.45986°N
ST2	99.80501°E	6.45015°N
ST3	99.78993°E	6.44026°N
ST4	99.77510°E	6.42988°N
ST5	99.81005°E	6.47013°N
ST6	99.79521°E	6.46013°N
ST7	99.78026°E	6.45013°N
ST8	99.76491°E	6.44013°N
ST9	99.75051°E	6.43003°N
ST10	99.80025°E	6.47998°N
ST11	99.78503°E	6.46986°N
ST12	99.77020°E	6.46013°N
ST13	99.75498°E	6.45000°N
ST14	99.73991°E	6.44002°N

TABLE 3. Recovery test results (concentration of Fe is in percentage (%), while other metals are in mg/kg dry weight)

Heavy metals	Measured SRM	Certified value	Recovery (%)
Iron, Fe	1.953 ± 0.115 %	2.008 ± 0.039 %	97.26
Arsenic, As	5.874 ± 0.124	6.23 ± 0.21	94.29
Cadmium, Cd	0.137 ± 0.011	0.148 ± 0.007	85.81
Cobalt, Co	4.226 ± 0.028	5.000	84.52
Chromium, Cr	32.764 ± 0.035	40.9 ± 1.9	80.11

where C_e is the concentration of the heavy metal in sediment samples; and C_b is the background values for the heavy metal. The listed background concentration (C_b) values in mg/kg were taken from Bodek et al. (1988), Carmichael (1989) and Ronov and Yaroshevsky (1972), as published by Lide (2004); Fe (5.63%), As (1.8), Cd (0.15), Co (25) and Cr (102). As for the degree of contamination, C_d is defined as the sum of all contamination factors for various heavy metals.

$$C_d = \Sigma C^i_f$$

The resulting values were then referred to the contaminant categories proposed by previous researcher (Dehghan Madiseh et al. 2009; Hakanson 1980) to show and acknowledge the contamination factor and pollution level of the studied heavy metals, as shown in Table 2.

TABLE 2(a). Contamination factor (C_f) index classification

C_f range Value	Classification
$C_f < 1$	low contamination factor
$1 \le C_f < 3$	moderate contamination factor
$3 \le C_f < 6$	considerable contamination factor
$C_f \ge 6$	very high contamination factor

TABLE 2(b). Degree of Contamination (C_d) index classification

C_d range Value	Classification
$C_d < 7$	low degree of contamination
$7 \le C_d < 14$	moderate degree of contamination
$14 \le C_d < 28$	considerable degree of contamination
$C_d \ge 28$	very high degree of contamination

RESULTS AND DISCUSSION

SPATIAL DISTRIBUTION OF HAZARDOUS HEAVY METALS IN SURFACE SEDIMENT OF DANGLI WATERS

The concentrations of all hazardous heavy metals are shown in Table 3. In general, the highest value of Fe and Cd were observed at ST4, while As, Co and Cr showed higher concentrations at ST7, ST8 and ST12, respectively. The annual average concentration of heavy metals in surface sediment of Dangli Waters, represented in decreasing order, is as follows; Fe>Cr>As>Co>Cd. According to the statistical analysis of two-way ANOVA, there was a significant difference between the sampling stations (p<0.05) for all heavy metals accept Co.

Apparently, the concentrations of Fe in the study area were constantly distributed to all sampling stations (Figure 2(a)) with the standard deviation value being less than 1%. According to Table 4, the concentration of Fe seemed higher compared to other metals. The maximum concentration of Fe reached 4.20±0.45% dry weight in ST4, while the minimum value recorded 2.46±0.46% dry weight in ST2. However, Cr obtained the second highest spot in heavy metal concentration with an average value of 76.18±11.68 mg kg^{-1} dry weight while displaying a uniform trend of distribution throughout all stations. Meanwhile, the average concentrations of both As and Co in this study area were discovered to be slightly lower than the earth's crust value, with the average concentration of 11.42±1.63 and 9.47±2.74 mg kg^{-1} dry weight, respectively. Last but not least, the concentration of Cd in the study area was indicated to be higher in some stations with the value of 0.20 (ST8) and 0.19 (ST4) mg kg^{-1} dry weight during SWM and FIM, correspondingly.

From observation, most of the higher profiles of heavy metal concentrations were obtained near to the cement plant production area (Figure 2). However, all metals except As (in some stations) were indicated to be lower than that of the world average of earth crust. The high concentrations of As in this study might have been incorporated with the cement plant production and agricultural activities around this study area. According to Bissen and Frimmel (2003), the ultimate source of As comes from human activities such as mining, smelter and pesticide application, but natural sources can also contribute to the As level in marine environment. Apart from that, the presence of heavy metals in the composition of clinker and cement are undeniable. According to Achternbosch et al. (2003), the amount of As and Cd introduced by the primary raw material in cement production is estimated to be 75% and <55%, correspondingly. Therefore, it is not surprising that the distribution of these heavy metals within the study area was found to be higher in areas adjacent to the cement plant. Furthermore, Sánchez-Rodas et al. (2005) found that the source of As comes from the discharge of a Cu

TABLE 4. The average, minimum and maximum concentration of heavy metals in the surface sediment of Dangli Waters

Station	Fe (%)	As (mg kg^{-1} dry weight)	Cd (mg kg^{-1} dry weight)	Co (mg kg^{-1} dry weight)	Cr (mg kg^{-1} dry weight)
ST 1	2.90±0.18 (2.65-3.06)	10.94±0.54 (10.26-11.58)	0.06±0.01 (0.05-0.07)-0.07)	7.54±1.08 (6.38-8.89)	68.48±0.71 (67.59-69.34)
ST 2	2.46±0.46 (2.03-3.06)	9.27±0.53 (8.54-9.73)	0.04±0.01 (0.04-0.05)	7.73±3.39 (4.90-11.92)	55.47±0.99 (54.59-56.83)
ST 3	3.86±0.69 (3.06-4.73)	12.62±0.87 (11.64-13.74)	0.07±0.01 (0.06-0.080	9.53±3.82 (7.20-15.21)	74.41±12.62 (55.52-81.77)
ST 4	4.20±0.45 (3.86-4.85)	13.92±1.61 (12.56-15.84)	0.11±0.06 (0.07-0.19)	11.58±3.12 (9.16-16.02)	89.93±1.70 (88.40-92.29)
ST 5	2.81±0.31 (2.36-3.02)	9.99±0.66 (9.37-10.84)	0.05±0.004 (0.05-0.06)	9.91±6.65 (5.83-19.85)	67.83±0.99 (66.94-69.19)
ST 6	3.75±0.47 (3.20-4.35)	11.66±1.27 (10.67-13.42)	0.05±0.01 (0.04-0.07)	8.20±2.09 (6.62-11.14)	67.77±15.61 (44.39-76.63)
ST 7	4.01±0.30 (3.63-4.34)	13.32±2.24 (11.76-16.63)	0.08±0.05 (0.05-0.16)	10.01±0.76 (9.09-10.94)	86.33±1.70 (84.80-88.69)
ST 8	3.96±0.20 (3.75-4.16)	11.52±1.05 (10.42-12.87)	0.11±0.08 (0.04-0.20)	11.94±3.67 (8.60-15.46)	79.35±0.99 (78.47-80.71)
ST 9	3.67±0.75 (3.03-4.64)	11.26±2.17 (9.03-14.25)	0.06±0.02 (0.04-0.09)	8.92±1.74 (7.50-11.36)	65.39±5.65 (57.01-69.25)
ST 10	3.45±0.29 (3.21-3.81)	11.33±0.62 (10.76-11.98)	0.07±0.01 (0.06-0.08)	9.28±1.07 (8.20-10.72)	83.21±0.99 (82.33-84.57)
ST 11	3.36±0.72 (2.47-4.00)	11.61±0.67 (11.02-12.58)	0.05±0.01 (0.04-0.06)	9.58±0.35 (9.15-10.01)	83.81±0.99 (82.92-85.16)
ST 12	3.95±0.48 (3.27-4.35)	11.70±1.87 (9.83-14.26)	0.04±0.01 (0.03-0.05)	10.12±3.49 (6.12-14.64)	91.53±0.99 (90.65-92.89)
ST 13	4.04±0.42 (3.73-4.64)	10.35±1.23 (8.97-11.94)	0.10±0.03 (0.05-0.13)	9.20±0.44 (8.80-9.78)	82.71±1.70 (81.18-85.07)
ST 14	3.68±0.25 (3.46-4.04)	10.34±1.26 (8.84-11.87)	0.05±0.01 (0.04-0.06)	9.10±0.35 (8.68-9.54)	70.28±16.06 (46.23-79.47)
Average	3.58±0.63	11.42±1.63	0.07± 0.03	9.47±2.74	76.18±11.68

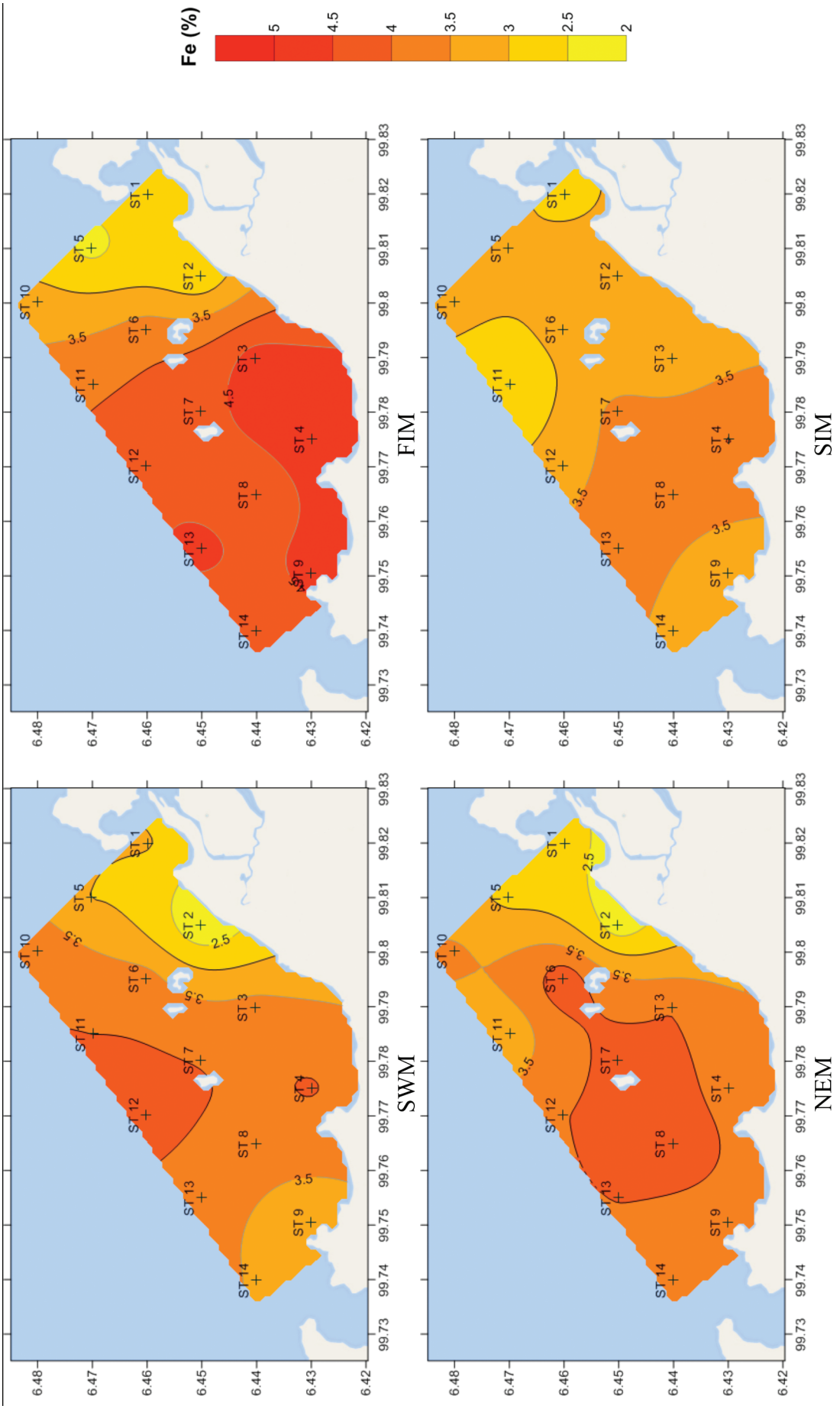

FIGURE 2(a). Fe concentration in concentration of heavy metals in the surface sediment of Dangli Waters

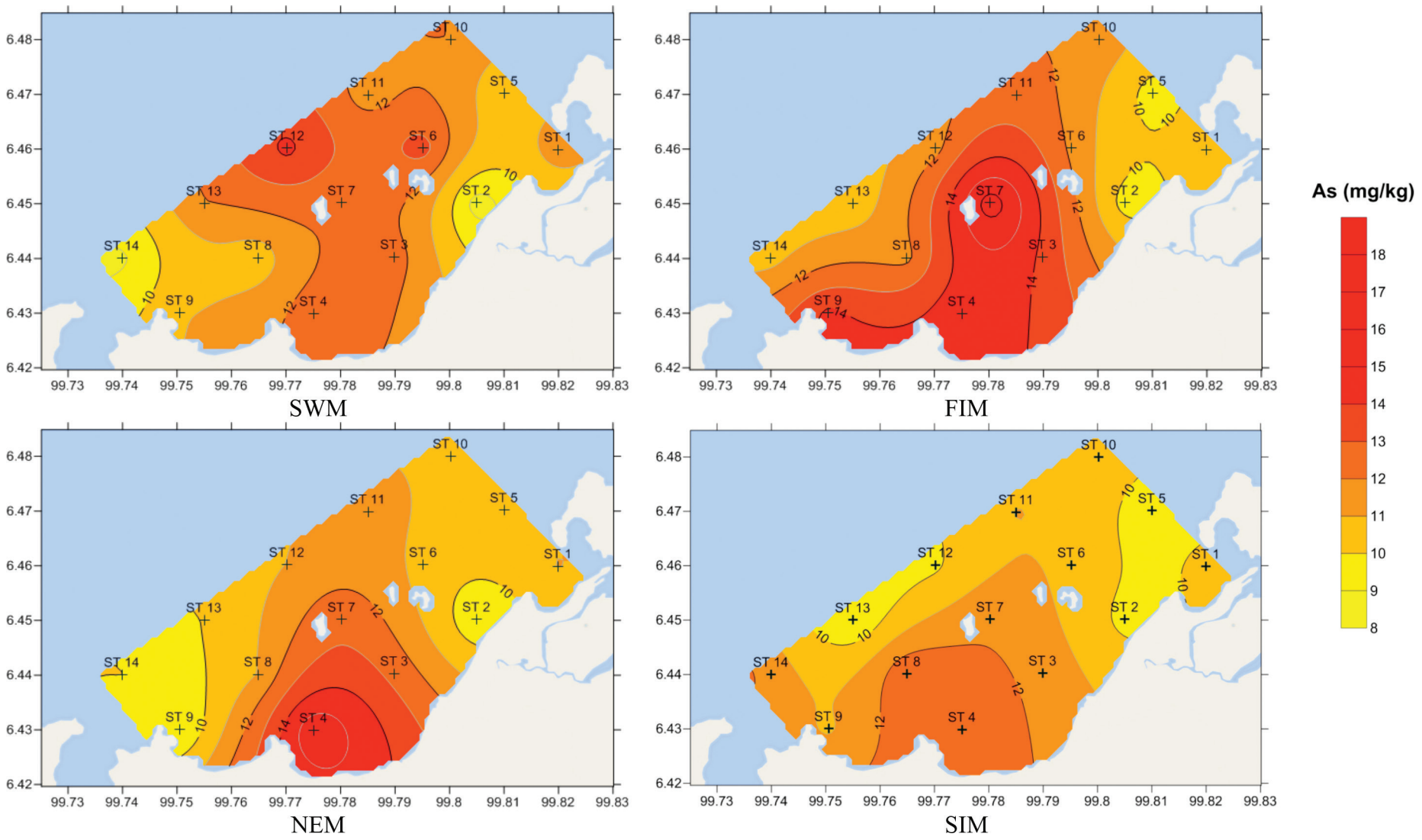

FIGURE 2(b). As concentration in concentration of heavy metals in the surface sediment of Dangli Waters

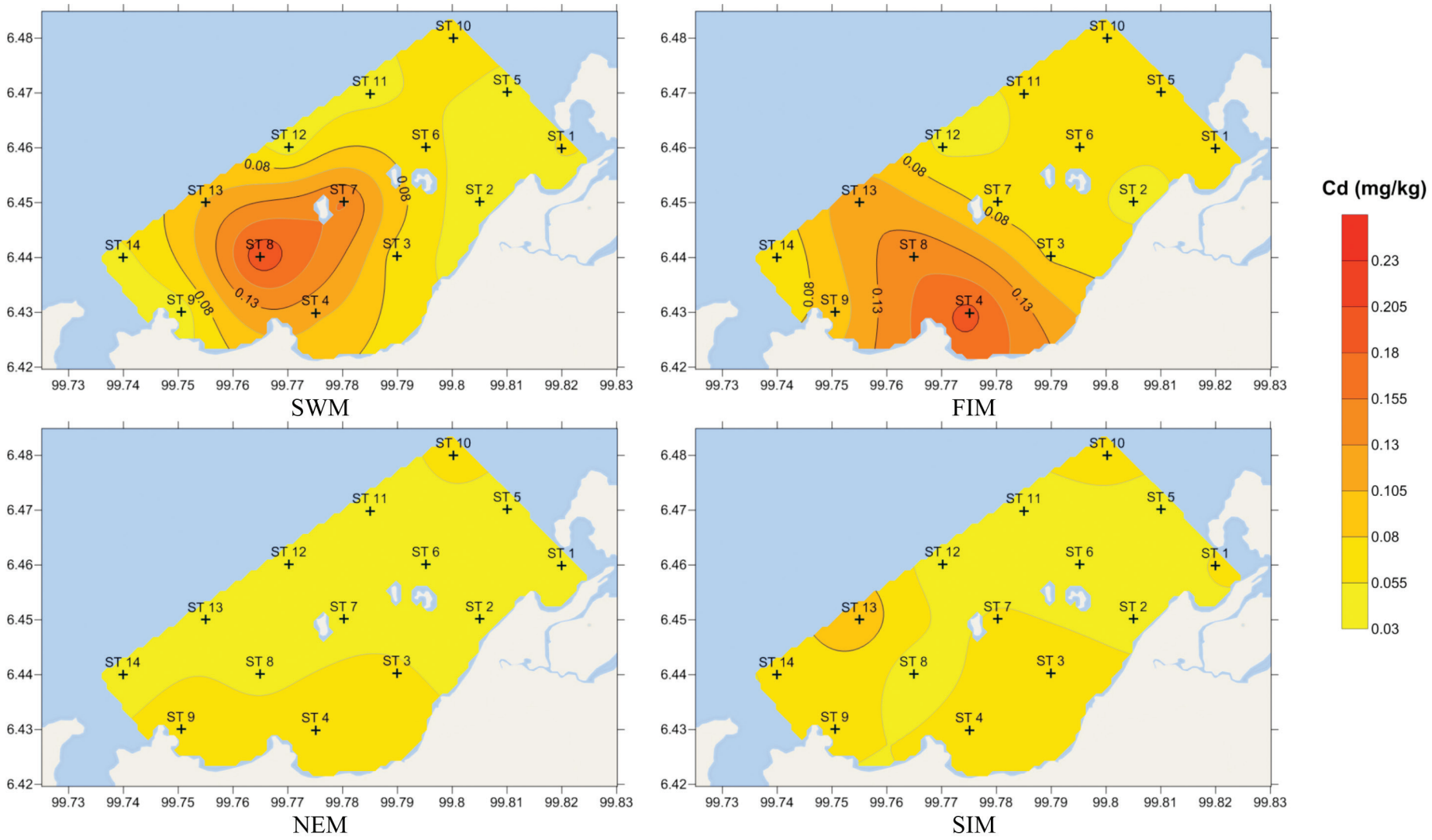

FIGURE 2(c). Cd concentration in concentration of heavy metals in the surface sediment of Dangli Waters

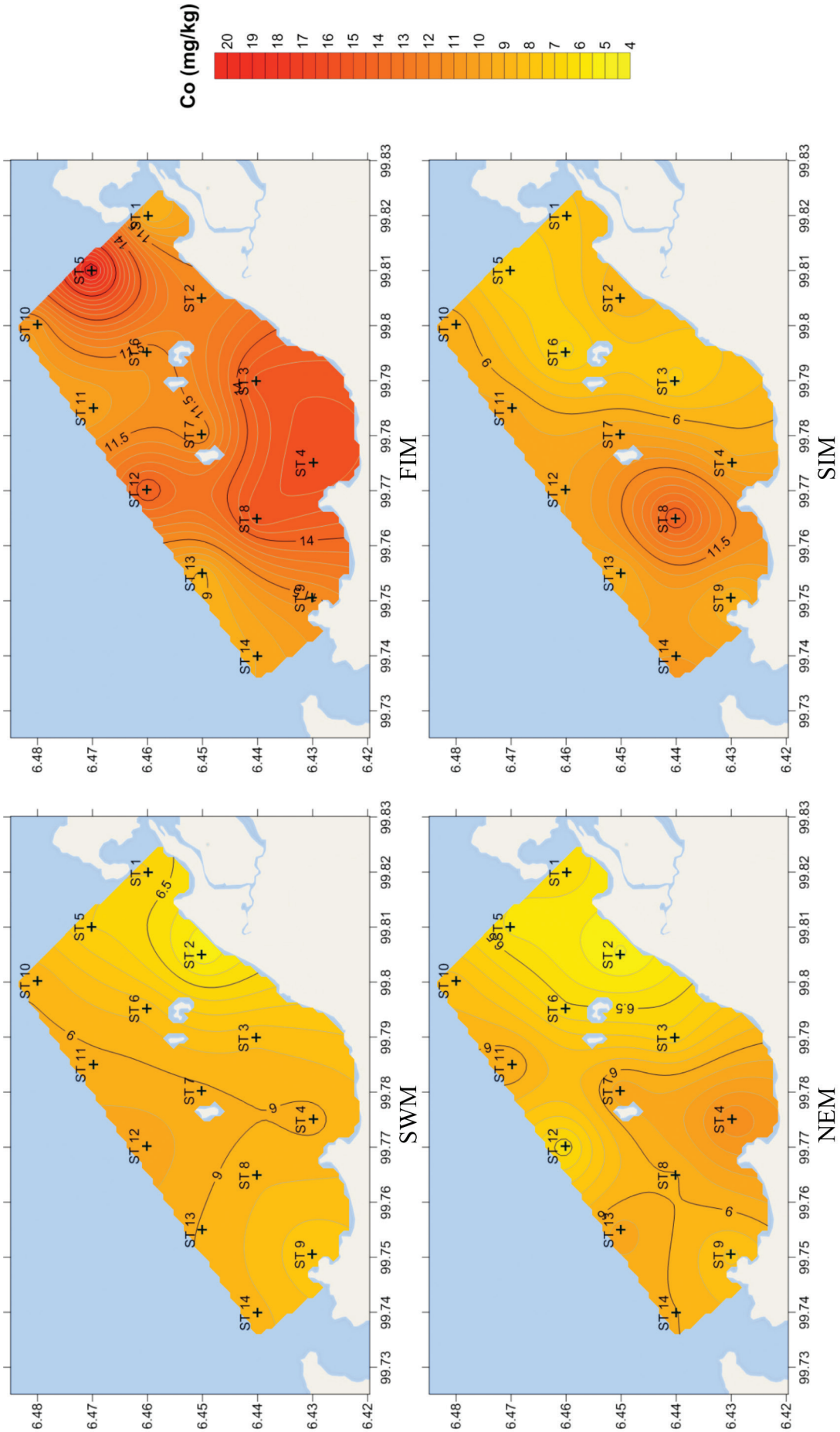

FIGURE 2(d). Co concentration in concentration of heavy metals in the surface sediment of Dangli Waters

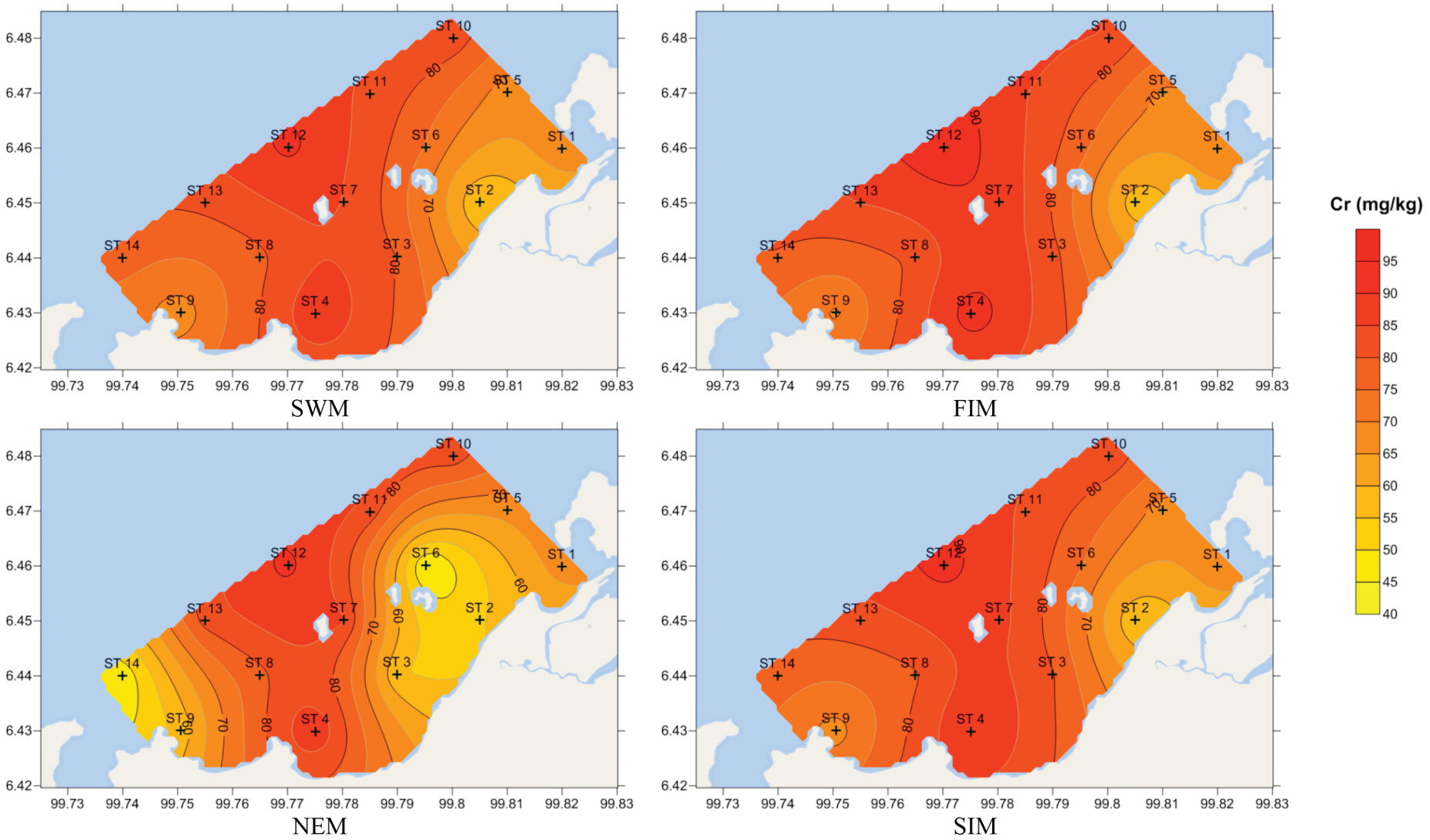

FIGURE 2(e). Cr concentration in concentration of heavy metals in the surface sediment of Dangli Waters

smelter which produced the highest arsenate (AsO_4^{3-}) level and a significant amount of arsenite (As_2O_3). Sukreeyapongse et al. (2009) stated that As contamination was first recognized in Ron Phibun District, Nakhon Si Thammarat Province, Thailand in the year 1987, with concentrations ranging between 2.53 and 151 mg/kg. Therefore, people who lived near or in old mining areas were sick with their skin turning black, and were later diagnosed as having skin cancer.

Other than that, the use of fertilizers in agriculture activities and golf course fields might be a contributing factor to the increase of Cd in the study area. The main anthropogenic sources of Cd in cultivated soils are phosphorus-fertilizers, atmospheric deposition, animal manures, and to a smaller extent liming agents, sewage sludge and biowaste (Louekari et al. 2000). Rukun and Liming (1992) reported that the phosphate fertilizers were generally the major source of trace metals among all inorganic fertilizers, and much attention had also been paid to the concentration of Cd in phosphate fertilizers. A great majority of agricultural soils in Malaysia are heavily fertilized by this kind of fertilizers (Zarcinas et al. (2004). According to Jamil et al. (2011), the total Cd concentration in the paddy soil samples obtained from Yan, Kota Setar, Kubang Pasu and Bumbung Lima, ranged from 3.54 to 20.86 mg/kg.

The comparison of heavy metal concentrations in marine sediment between present study area and other Asian coastal areas is available in Table 5. Based on this table, the average heavy metal concentrations in Dangli Waters seemed to be similar to those of coastal sediments from other places in Langkawi, Malaysia and even some other Asian countries. However, As concentration in the present study area was found to be relatively higher compared to the earth's bulk continental crust, but still lower compared to the Jakarta Bay.

SEASONAL VARIATION OF HAZARDOUS HEAVY METALS IN SURFACE SEDIMENT OF DANGLI WATERS

As a whole, the concentrations of all hazardous heavy metals were defined as higher in surface sediment during FIM season compared to the other seasons (SWM, NWM, and SIM). This result was in the line with the finding by Ciszewski (2001) and Fortune (2006) where flood water from terrestrial areas has increase the heavy metal loads and deposition compared to background levels. From this study, the order of heavy metal concentration in Dangli Waters remained similar during all three seasons (SWM, NEM, and SIM seasons) where Fe>Cr>As>Co>Cd. However, the order seemed to have slightly changed during FIM season, where Fe>Cr>Co>As>Cd. The slight changes may have occurred due to heavy rainfall during this period where terrestrial fine sediment and clay were brought and deposited into this area. According to Franky et al. (2011) and Hamilton (1994), Co may occur naturally in the soil and its concentration depends on the composition of organic matter and clay.

According to Figure 2, a large contrast in distribution for most of the studied heavy metals was seen during SWM and FIM. Some stations such as ST4, ST7 and ST8 experienced dramatic changes in heavy metal distribution. The varying distribution of heavy metals in the study area can be explained by the wet weather condition during the sampling period with high water runoff from the Langkawi terrestrial areas, leading to the increase of sediment deposition into the Dangli Waters. Statistically, there was a significant difference among seasons for each of the metals ($p<0.05$). According to Dehghan Madiseh et al. (2009), significant changes in surface sediment occurring in a short period of time was uncommon. Nevertheless, taking into account the dynamic nature process of the marine environment such as the source of pollution, strong tidal circulation, high sedimentation

TABLE 5. The comparison of heavy metal concentrations between present study and other heavy metal studies throughout Langkawi UNESCO Global Geopark, Asian country and world average of earth crust

No.	Area	As (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Fe (%)	References
A	Langkawi UNESCO Global Geopark						
	Dangli Waters	11.42±1.63	0.07± 0.03	9.47±2.74	76.18±11.68	3.58±0.63	Present Study
	Sungai Kilim	-	0.27 ± 0.14	7.69 ± 0.82	-	4.80 ± 0.42	Jamil and Mohd Lias (2013)
	Langkawi Coastal Area	-	0.34 - 1.1	-	45.65 - 76.15	-	Mohdzahir et al. (2012)
	Pulau Payar	-	-	-	4.50	-	Mokhtar et al. (2001)
	Langkawi South Coastal Area	-	-	13-75	2-26	-	Idris et al. (2009)
	Teluk Ewa Cement Plant	-	0.01-0.06	1.52-3.80	-	-	Franky et al. (2011)
B	Asian Country						
	Jakarta Bay, Indonesia	<LOD-69	<LOD-13	-	<LOD-951	-	Siregar et al. (2016)
	Thailand Gulf, Thailand	-	-	17–716	27–1104	-	Censi et al. (2006)
	Tekong, Singapore	-	0.05–0.07	-	-	-	Chakraborty et al. (2014)
C	World Average of Earth Crust						
	Earth Bulk Continental Crust	1.8	0.15	25	102	5.63	Lide (2004)

rates and rainfall distribution (seasonal), the variation in distribution among heavy metals in Dangli Waters may be possible.

ENVIRONMENTAL RISK ASSESSMENT

The contamination factor (C_f) and degree of contamination (C_d) were calculated to obtain the pollution status of marine sediment in Dangli Waters. According to Table 6, the range of C_f values in the investigated sediments were 0.44-0.75 for Fe, 5.15-7.73 for As, 0.27-0.73 for Cd, 0.30-0.48 for Co and 0.54-0.90 for Cr. The order of heavy metal contamination factor in Dangli Waters is as follows; As>Cr>Fe>Cd>Co. However, looking at the degree of contamination, the difference shown between the studied stations is according to the following descending order;

TABLE 6. Contamination factor of different metals (C_f) and degree of contamination level (C_d), in Dangli Waters

Stations	Contamination factor (C_f)					Degree of contamination (C_d)
	Fe	As	Cd	Co	Cr	
ST 1	0.52 $C_f < 1$ Unpolluted	6.08 $C_f > 6$ Highly Polluted	0.38 $C_f < 1$ Unpolluted	0.30 $C_f < 1$ Unpolluted	0.67 $C_f < 1$ Unpolluted	7.94 $7 \leq C_d < 14$ Moderate
ST 2	0.44 $C_f < 1$ Unpolluted	5.15 $3 \leq C_f < 6$ Polluted	0.30 $C_f < 1$ Unpolluted	0.31 $C_f < 1$ Unpolluted	0.54 $C_f < 1$ Unpolluted	6.74 $C_d < 7$ Low
ST 3	0.69 $C_f < 1$ Unpolluted	7.01 $C_f > 6$ Highly Polluted	0.44 $C_f < 1$ Unpolluted	0.38 $C_f < 1$ Unpolluted	0.73 $C_f < 1$ Unpolluted	9.25 $7 \leq C_d < 14$ Moderate
ST 4	0.75 $C_f < 1$ Unpolluted	7.73 $C_f > 6$ Highly Polluted	0.73 $C_f < 1$ Unpolluted	0.46 $C_f < 1$ Unpolluted	0.88 $C_f < 1$ Unpolluted	10.55 $7 \leq C_d < 14$ Moderate
ST 5	0.50 $C_f < 1$ Unpolluted	5.55 $3 \leq C_f < 6$ Polluted	0.33 $C_f < 1$ Unpolluted	0.40 $C_f < 1$ Unpolluted	0.66 $C_f < 1$ Unpolluted	7.44 $7 \leq C_d < 14$ Moderate
ST 6	0.67 $C_f < 1$ Unpolluted	6.48 $C_f > 6$ Highly Polluted	0.37 $C_f < 1$ Unpolluted	0.33 $C_f < 1$ Unpolluted	0.66 $C_f < 1$ Unpolluted	8.50 $7 \leq C_d < 14$ Moderate
ST 7	0.71 $C_f < 1$ Unpolluted	7.40 $C_f > 6$ Highly Polluted	0.56 $C_f < 1$ Unpolluted	0.40 $C_f < 1$ Unpolluted	0.85 $C_f < 1$ Unpolluted	9.91 $7 \leq C_d < 14$ Moderate
ST 8	0.70 $C_f < 1$ Unpolluted	6.40 $C_f > 6$ Highly Polluted	0.73 $C_f < 1$ Unpolluted	0.48 $C_f < 1$ Unpolluted	0.78 $C_f < 1$ Unpolluted	9.09 $7 \leq C_d < 14$ Moderate
ST 9	0.65 $C_f < 1$ Unpolluted	6.25 $C_f > 6$ Highly Polluted	0.43 $C_f < 1$ Unpolluted	0.36 $C_f < 1$ Unpolluted	0.64 $C_f < 1$ Unpolluted	8.34 $7 \leq C_d < 14$ Moderate
ST 10	0.61 $C_f < 1$ Unpolluted	6.29 $C_f > 6$ Highly Polluted	0.45 $C_f < 1$ Unpolluted	0.37 $C_f < 1$ Unpolluted	0.82 $C_f < 1$ Unpolluted	8.55 $7 \leq C_d < 14$ Moderate
ST 11	0.60 $C_f < 1$ Unpolluted	6.45 $C_f > 6$ Highly Polluted	0.33 $C_f < 1$ Unpolluted	0.38 $C_f < 1$ Unpolluted	0.82 $C_f < 1$ Unpolluted	8.58 $7 \leq C_d < 14$ Moderate
ST 12	0.70 $C_f < 1$ Unpolluted	6.50 $C_f > 6$ Highly Polluted	0.27 $C_f < 1$ Unpolluted	0.40 $C_f < 1$ Unpolluted	0.90 $C_f < 1$ Unpolluted	8.77 $7 \leq C_d < 14$ Moderate
ST 13	0.72 $C_f < 1$ Unpolluted	5.75 $3 \leq C_f < 6$ Polluted	0.64 $C_f < 1$ Unpolluted	0.37 $C_f < 1$ Unpolluted	0.81 $C_f < 1$ Unpolluted	8.29 $7 \leq C_d < 14$ Moderate
ST 14	0.65 $C_f < 1$ Unpolluted	5.74 $3 \leq C_f < 6$ Polluted	0.32 $C_f < 1$ Unpolluted	0.36 $C_f < 1$ Unpolluted	0.69 $C_f < 1$ Unpolluted	7.77 $7 \leq C_d < 14$ Moderate

ST4>ST7>ST3>ST8>ST12>ST11>ST10>ST6>ST9 >ST13>ST1>ST14>ST5>ST2

This finding is in agreement with the cluster analysis of Bray Curtis similarity, based on the C_f values which classified the heavy metals into two groups of different contamination levels; 'Unpolluted' for Fe, Cd, Co and Cr, and, 'Highly Polluted' for As (Figure 3(a)). However, based on spatial distribution, all stations indicate moderate degree of contamination, except for ST2 which showed a C_d value of less than 7 (Figure 3(b)).

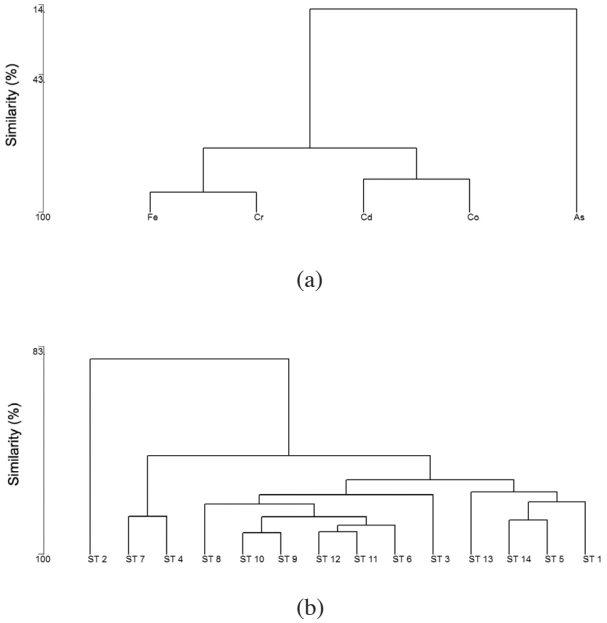

FIGURE 3. The dendrogram cluster analysis for Bray Curtis similarity, 'a' based on C_f of different heavy metals and 'b' based on average values of heavy metals concentration in sediment for each studied station

CONCLUSION

In present study, the heavy metal contamination in Dangli Waters differed between the considered metals and concentrations of all studied heavy metals also vary between seasonal changes. The concentrations of most heavy metals were lower during the dry season (NEM) and slightly higher during the wet season (FIM). However, during this season, the wash load and suspended load from the terrestrial water runoff are indistinguishable. Furthermore, the distribution of heavy metals around these waters was in the decreasing order of Fe>Cr>As>Co>Cd. Metals such as As, should be the main concern due to the C_f values which signified significant polluted with the average value of 6.34±0.7. The higher concentration of As might be due to the presence of a cement plant production. However, the degree of contamination level (C_d) for the whole study area was obtained in moderate state (8.55± 0.97). Therefore, mitigation measures must be formed to preserve and conserve these waters from the dangers of these harmful pollutants. In order to prevent further spreading of pollutants, these waters can be gazetted as a conservation zone under the Malaysian Fisheries Act 1985. With the establishment of this zone, our National water quality index can be further enhanced from Level II (the existing) to Level I, for the purpose of marine habitat conservation. Therefore, a continuous study on heavy metal observation should be carried out to continuously gain and provide basis information for assessments of our coral reef status and ultimately, for aiding management and conservation decisions of our national guardians.

ACKNOWLEDGEMENTS

This research was conducted under the funding of Langkawi Development Authority (LADA) through the Field Study Grant. The author wishes to express their gratitude to the UiTM Oceanography laboratory members for their invaluable assistance and hospitality throughout the sampling period.

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Received: 6 February 2017
Accepted: 30 August 2018