Vertical Distribution of Heavy Metals in Coastal Sediment: A Record of the Changing Input in the Estuarine of the Semarang Flood Canal

Distribusi Vertikal Logam Berat dalam Sedimen Pesisir: Rekaman atas Perubahan Masukan di Estuari Banjir Kanal, Semarang

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(Received 02 Februari 2018; in revised form 14 Februari 2018 accepted 30 April 2018)

ABSTRACT: Sediment plays an important role in archiving contaminant like heavy metals and could record metal contamination in sediment due to land-based input such as flood canals of Semarang. This study was to understand the changing record of heavy metals' contamination in coastal sediment and to assess the sediment quality. Two core sediments, from two different sites, were collected up to 80 cm in depth and, subsequently, sectioned within a 5 cm interval. A digestion system followed by AAS measurement, was used to determine the metal concentrations, Enrichment Factor (EF) was applied to assess sediment quality. The sediment fraction and metals concentration revealed the changing of input and deposition process along sediment cores in East Flood Canal (EFC) and West Flood Canal (WFC). There was an alteration of sediment composition in which the proportion of sediment composition moved to finer size in EFC and a pulse of coarser-finer-coarser size of sediment composition was observed in WFC. In general, higher concentrations of Fe, Cd, Cu, Ni and Zn were observed differently with Pb concentration. Ni along both sediment cores was unenriched (EF<1), whereas Cd, Cu, Pb, and Zn were classified minor to moderate enrichment. Thus, the source and deposition processes of these Fe, Cd, Cu, Ni and Zn were different compared with those of Pb.

Keyword: flood canal, Semarang, heavy metal, Enrichment Factor

ABSTRAK: *Sedimen memiliki peran sebagai tempat penyimpanan bahan pencemar seperti logam berat dan studi atas pencemaran logam berat dalam sedimen di banjir kanal kota Semarang belum banyak dilakukan. Sehingga tujuan dari penelitian ini adalah untuk mengetahui sejarah pencemaran dengan melihat distribusi vertikal kemudian menilai status logam berat dalam sedimen di muara banjir kanal barat dan banjir kanal timur kota Semarang. Untuk menjawab tujuan penelitian, telah dilakukan pengambilan 2 sampel sedimen inti hingga kedalaman 80 cm kemudian sedimen tersebut diambil tiap interval 5 cm. Metode peleburan yang diikuti pengukuran dengan AAS dilakukan untuk mengukur konsentrasi logam dan Enrichment Factor (EF) dihitung untuk menilai kualitas sedimen. Fraksi sedimen dan konsentrasi logam berat menunjukkan perubahan masukan dan proses deposisi di sepanjang sedimen inti yang dianalsis dari Banjir Kanal Timur (BKT) dan Banjir Kanal Barat (BKB). Tampak adanya perubahan komposisi sedimen dimana sedimen di EFC cenderung menjadi lebih halus sementara tampak adanya fluktuasi komposisi sedimen di WFC dari kasar-halus-kasar. Masing-masing logam menunjukkan pola yang berbeda walaupun konsentrasi Fe, Cd, Cu , Ni dan Zn tinggi tampak di periode energi yang lebih tinggi dan konsentrasi Pb tinggi teramati sema periode energi rendah. Ni di kedua sedimen inti masih berada pada konsentrasi alami (EF<1),tetapi Cd, Cu, Pb dan Zn telah mengalami pengayaan minor hingga moderat. Informasi tersebut dapat menunjukkan sumber dan proses deposisi Fe, Cd, Cu, Ni dan Zn berbeda dengan Pb.*

Kata kunci: *Banjir kanal, Semarang, logam berat, Enrichment Factor.*

INTRODUCTION

The rapid growth of human population in recent decades requires the environmental support, hence, the demand for natural resources inclines. However, the massive exploitation, without a proper management, can gradually cause their depletion (Bingöl *et al.*, 2013; Raize *et al.*, 2004; and Ribeiro *et al.*, 2017). The second problem is that their utilization has also generated the waste (Thévenot *et al.*, 2007; Wang *et al.*, 2012). Heavy metals, contained waste discharge, are considered as persistent, toxic and bioaccumulative triggering a metabolism disturbance in certain dose (Pekey, 2006; Zhang *et al.*, 2017).

In the aquatic environment, heavy metal presents in both dissolved and particulate phase (Sakellari *et al.*, 2011). In an estuary, a region of the mixing of fresh water and sea water, those phases tend to change (Mukherjee, 2014). It is due to such complex processes involving adsorption-desorption, chemical reaction, and other physical processes prior to the metal deposition towards the bottom sediment bed (Chakraborty *et al.*, 2014). The metals continuously and stratigraphically deposit and will be preserved to generate heavy metal archive in sediment. The analysis of vertical distribution of heavy metals in sediment cores provides valuable information to describe the historical record of heavy metals deposition during some period of time (Huang and Lin, 2003; Mukherjee, 2014; and Zorer *et al.*, 2008).

Semarang, one of the Indonesian active port cities and the capital city of Central Java province in the north-middle part of Java Island, it has progressively developed in population growth and industry. As regard to its location and topography, annual flood occurs, and two flood canals sandwiching the city have been developed as the mitigation effort (Suyarso and Susana, 2010). Like other rivers, flood canal transports not only water but also pollutant such as heavy metals. This study was to understand the historical records of heavy metals' contamination based on their vertical distribution and assessing the sediment quality based on those metal concentrations.

MATERIAL AND METHODS

Sample collection

In order to collect sediment sample based on its stratigraphy, sediment core method was employed. Core samples were collected in the geographical position of 110.39° E and 6.95° S for West Flood Canal (WFC) and 110.45° E and 6.93° S for East Flood Canal (EFC) in April 2016 (Figure 1). Those locations were undisturbed points so the sediment was accumulated with minimum changes. The purpose of selecting that kind of location was to collect representative sediment. The sample from WFC was collected right in the river mouth however sediment from EFC was sampled sea-ward direction due to the topographic difficulties in the area.

The sediment was collected using Poly Vinyl Chloride (PVC) pipe, 4 cm in diameter and 2 m in length. That PVC pipe was then pushed down into bottom bed sediment at aforementioned points. The collected core sediment was then subsampled within 5 cm interval, 80 cm in total length of sediment core was collected in WFC (B point) and 65 cm in total length of sediment core was collected in EFC (T point). Those subsamples were then stored in PE box at 4°C in temperature following the sampling procedure of Loring and Rantala (1992).

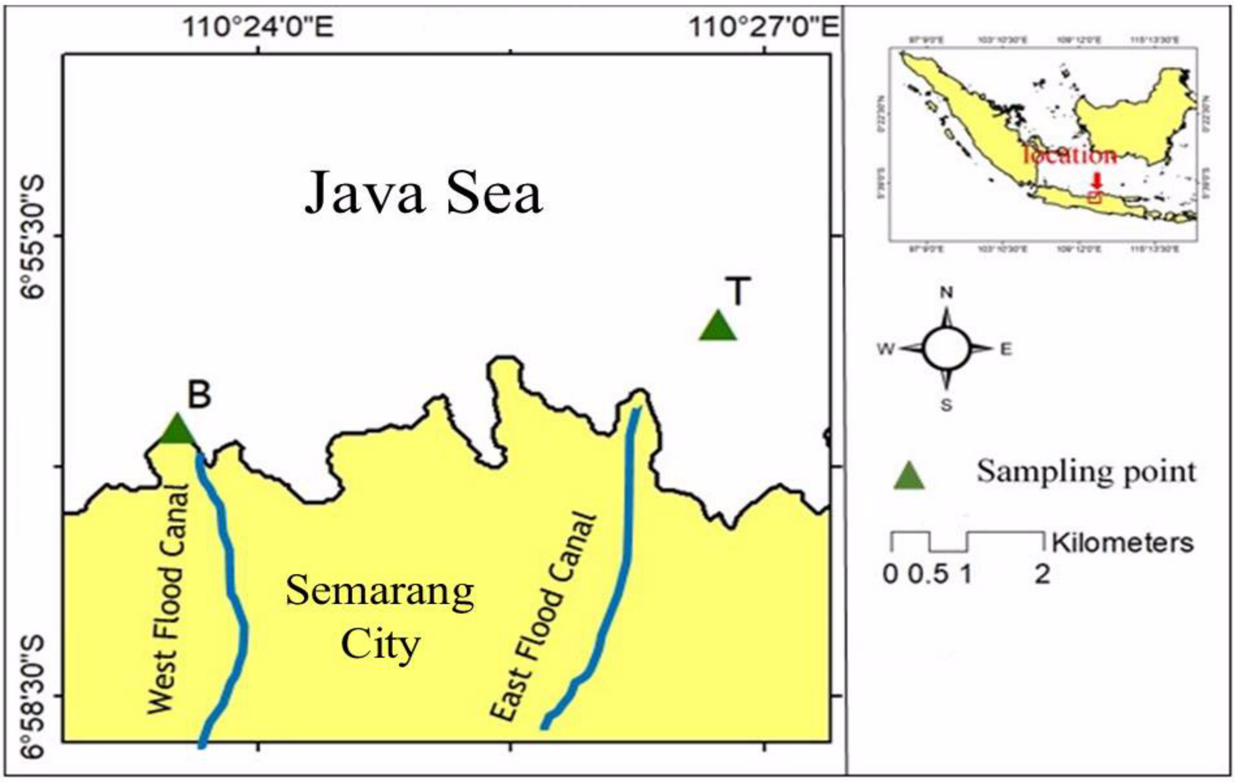

Figure 1. The location of sample collection in both East and West Flood Canal in Semarang.

Sediment texture analysis

The analysis of sediment size as one of the sediment characterization used in this study was following Wentworth scale (1922). Generally, the method was applying separation and gravimetric protocol. The sediment was sieving passing through a unit of separator and sediment was separated based on its size during this process. The calculation of the amount of each sediment size (as percentage) was then carried out based on the comparison of the weight of each separated sediment to the weight of initial sediment used.

Heavy metal analysis

The collected sediment samples were then analyzed using acid digestion procedure followed by the measurement using Flame Atomic Absorption Spectrophotometer in the Laboratory of heavy metals, Research Center for Oceanography-LIPI. The analysis was based on a dry basis. A gram of dry sediment was then digestion using a sequence of HNO_3, H_2O_2, and HCl under reflux system at 95±2 °C for 6 hours (USEPA 3050b methods). The digested sample was then measured using Flame Atomic Absorption Spectrophotometer Varian AA 20 plus®. All acid used in the analysis was pro-analytic grade manufactured by Merck, Germany. All glassware was pre-cleaned using HNO_3 1+1 for 24 hours before use.

Data Analysis

PCA analysis was computed to understand the correlation between sediment texture and metal concentration. Hence, in order to assess the condition of metals in sediment, Enrichment Factor (EF) was computed. The computation of EF was carried out by normalized the certain metal with background concentration. Fe concentration was used as a reference and metal concentration in the average crust was applied for background data. The EF was formulated as (El-Said *et al.,* 2014):

$$EF = \left[\frac{C_i}{C_r}\right]_{sample} \times \left[\frac{C_i}{C_r}\right]^{-1}_{background} \qquad (1)$$

Ci and *Cr* represented the concentration of specific metal i and concentration of the reference metal (Fe) in either sample or background data. According to Brady *et al.* (2014), *EF* score >1 is triggered by anthropogenic influence and El-Said *et al.* (2014) describe the interpretation of *EF* score as Table 1.

Table 1. The interpretation of EF score (El-Said *et al.,* 2014).

Score	Interpretation
EF <1	*no enrichment*
1 ≤ EF <3	*minor enrichment*
3 ≤ EF <5	*moderately enrichment*
5 ≤ EF <10	*moderately severe enrichment*
10≤ EF <25	*severe enrichment*
25 ≤ EF ≤ 50	*very severe enrichment*
EF > 50	*extremely severe enrichment*

RESULT

The vertical profile of sediment texture

The sediment in EFC and WFC was dominated by silt although a few differences were shown (Figure 2). For example, finer to coarser size particles were found in the surface sediment of WFC and finer size particle only was observed in surface sediment of EFC. In addition, sand size particle exhibited a fluctuation along the cores. Those changes in sediment composition implied the alteration of sediment input and its depositional process. The coarser sediment might associate with the deposition during higher energy period such as a strong sea current or strong riverine discharge. The finer sediment depicted the deposition happened during lower energy period or the deposition happened in slower process. In addition, the fluctuation of sediment size may also reflect the alteration of chemical composition like redox at the representative time since redox condition is associated with the presence of oxygen. Thus, the coarser size sediment easily allows oxygen to diffuse inside the bed implying more oxic state (Argese *et al.,* 1992).

WFC showed a pulse of sand composition indicating an increase and decrease of its amount. Higher composition of sand was observed at depth of 0-15 cm (top layer), 35-50 cm and 60-65 cm (bottom layer). Relatively lower composition of sand in WFC was observed at both 15-35 cm and 50-60 cm depth. These alternate occurrences indicate the changing of sediment deposition processes within this area.

Uniquely, EFC exhibited slightly difference in sediment composition. At the top layer to the 30 cm depth, sand was absent and the sediment was mainly composed by silt and clay resembling the lowest energy occurred at this depth. The fluctuation occurred below 30 cm depth with relatively low composition of sand size particle was observed at 40-65 cm depth. Thus, trend of energy reduction was observed to date.

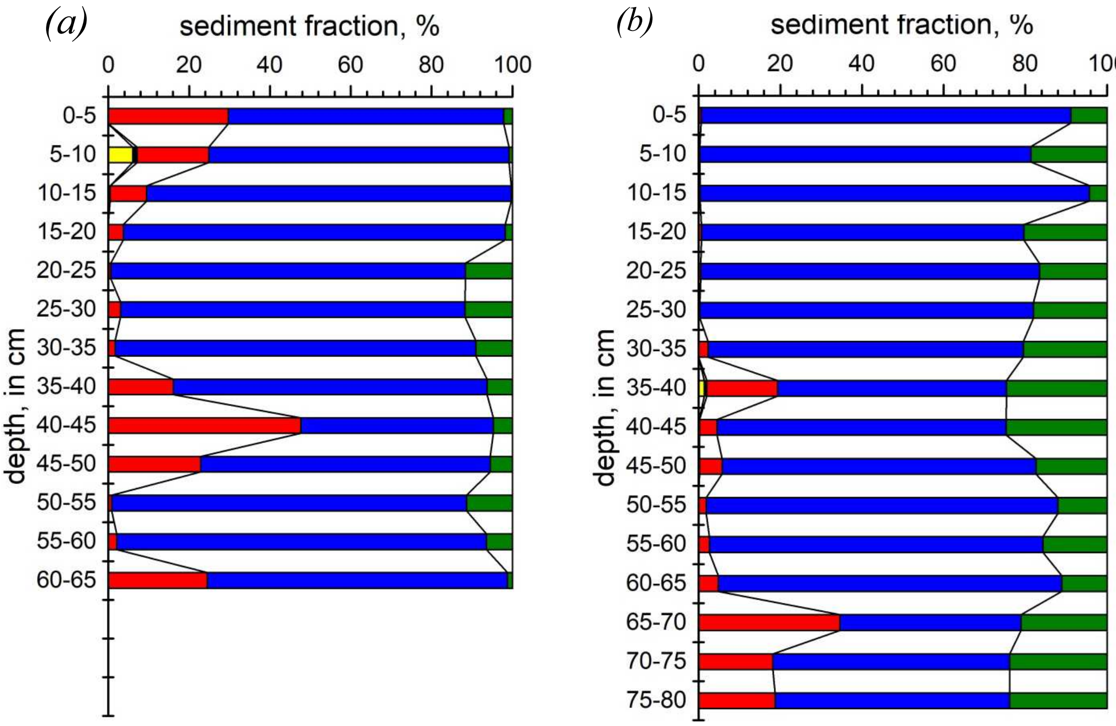

Figure 2. The vertical profile of sediment texture (a) WFC and (b) EFC. The color represented the fraction of sediment: ( ) clay, ( ) silt, ( ) sand, ( ) granule, and ( ) pebble.

Vertical distribution of Fe

The vertical distribution of Fe presented in Figure 3. The concentration of Fe increased from the top layer to bottom layer in EFC and vice versa in WFC. Fe in WFC tended to steeply increase in the recent layer yet the fluctuation was observed downward. Relatively lower concentration of Fe occurred at depth 15-30 cm and 45-60 cm. In contrast, relatively higher concentration of Fe observed at depth 0-15 cm, 35-45 cm and 60-65 cm.

In contrast, Fe concentration in EFC tended to increase downward and the fluctuation can be grouped into at least 3 periods i.e. low concentration in top layer (depth 0-25 cm), medium concentration (depth 30-60 cm) and high concentration (depth 60-85 cm). In addition to the effect of physical deposition (i.e. due to current velocity), metal deposition can also affected by chemical processes during deposition. The occurrence of Fe is related to the chemical environment e.g. the redox condition. In the reducing condition, Fe is in dissolved Fe^{2+} form, whereas it is in the precipitated Fe^{3+} in the oxidizing condition (Morita *et al.,* 2017). This suggests that the increasing Fe in WFC was due to oxic deposition, whereas it was more reducing in EFC. The oxic condition of the sediment could be derived from oxygen diffusion between sediment and overlying water. The increase of diffusion is easier in the coarse sediment compared with fine sediment. This seems to coincidence with the profile of sandy sediments in WFC that could probably more oxic condition in recent deposition, whereas chemical environment was more reducing in EFC due to more fine sediments that limit the oxygen diffusion. This could suggest that chemical deposition of Fe in WFC and EFC seems to be importance.

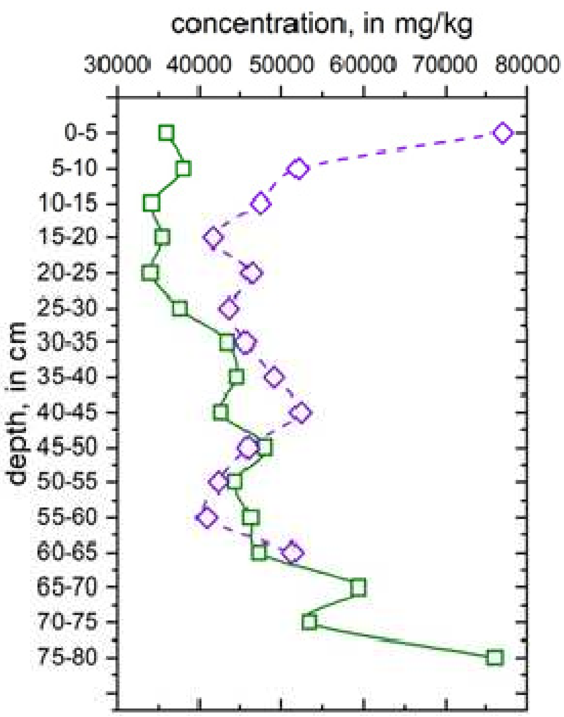

Figure 3. The vertical distribution of Fe in sediment in EFC (—□—) and WFC (- ◇ -) of Semarang City.

Vertical distribution of Cd

As presented in Figure 4, the vertical distributions of Cd in EFC and WFC were identical showing lower Cd concentration in the top layer. The low concentration of Cd both in EFC and WFC fell in almost similar value, 0.14-0.15 mg/kg and the occurrence of these low concentrations was predominant in both cores. The high concentrations of Cd were observed at the depth of 20-25 cm, 35-40 cm, 45-50 cm in WFC and at the depth of 15-20 cm, 35-40 cm, 55-60 cm in EFC. These high concentrations of Cd in both stations indicated the additional Cd input at time of their deposition and showed increasing in both stations implying that amount of Cd discharge was increasing. Since fossil fuel is noticed to be one of main Cd source (Hutton, 1983), Cd was suspected to come from any activities that utilized fossil fuel like vehicle, harbour and shipping activities around the area. The increasing pulse of Cd reflected the increasing volume of those activities.

The lower concentration of Cd in the top layer indicated the decrease of Cd deposition in the recent time in which no enrichment (EF<1) was observed at the top layer of WFC (0-10 cm), but minor enrichment (EF>1) at all top layers of EFC. Moving downward, a steep alteration of Cd input and the extremely high concentrations were observed at the depth of 20-25 cm in WFC (0.4 mg/kg) lead to minor enrichment (EF<3) and at 15-20 cm in EFC (0.5 mg/kg) lead to moderately enrichment (EF<5). Another increment was appeared at 35-40 cm depth in both EFC and WFC, and then followed by the decline. Overall, the sediment was considered at no enrichment to minor enrichment by Cd in EFC (EF score: 0.6-2.6). However, the sediment in WFC was moderately enriched by Cd (EF score: 0.5-4.3) at 20-25 cm in depth by Cd.

Vertical distribution of Cu

Figure 5 showed a variation of the vertical distribution of Cu in sediment. Cu in WFC was slightly varied and no exceptional fluctuation was observed. Referring to the profile of grain size sediment (Figure 2), the deposition of Cu in WFC and EFC was tend to correlated with fine sediment implying the fluctuation was affected by adsorption. Interestingly, below the depth 60 cm, Cu concentration increased during the higher energy period implying variety of deposition processes.

The Cu profile in WFC tended to vary slightly ranging from 25.9-36.7 mg/Kg indicating no major changes in Cu input. The sediment in WFC was unenriched by the fluctuation of Cu since EF score was 0.4-0.9 means no pollution of Cu was recorded in WFC. In contrast, it showed increasing downward from the top layer to the depth of 60-65 cm in EFC (25.6-59.5 mg/kg) then decreasing to the bottom layer indicating the decrease of Cu input. The sediment core from EFC was dominantly unenriched by Cu (EF<1). However, it was observed that during the increase of Cu input in EFC (depth at 30-35 cm, 45-50 cm, 55-65 cm) gave a consequence on minor enrichment (EF>1) so at that time, the sediment was slightly polluted by Cu.

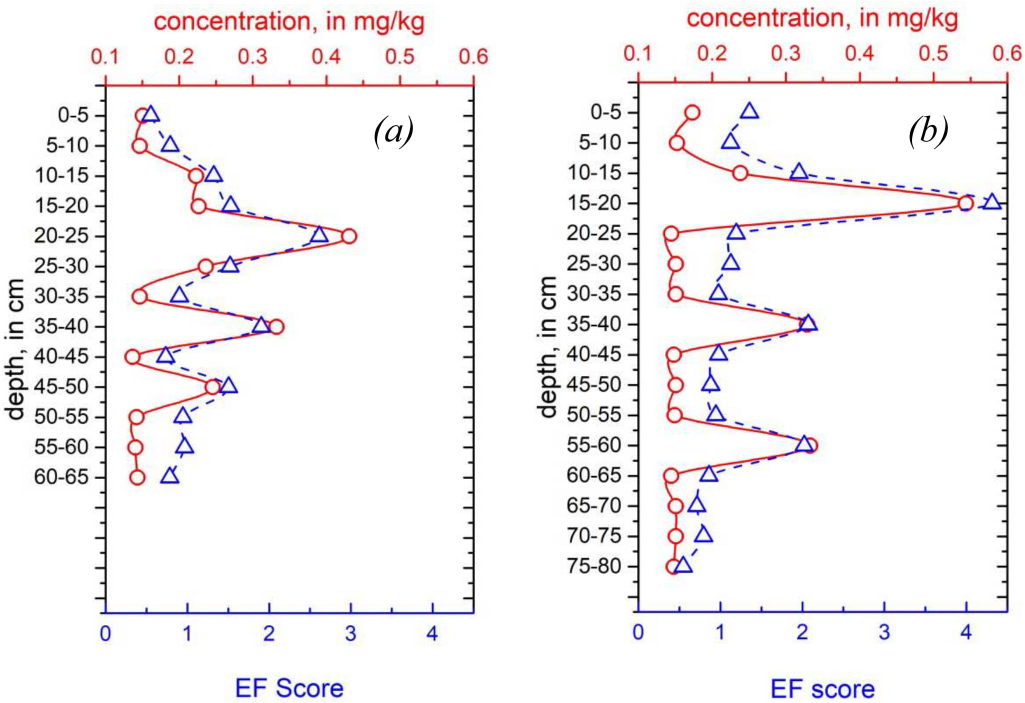

Figure 4. The vertical distribution of Cd (—o—) and EF score for Cd (- -△- -): (a) WFC and (b) EFC in Semarang City.

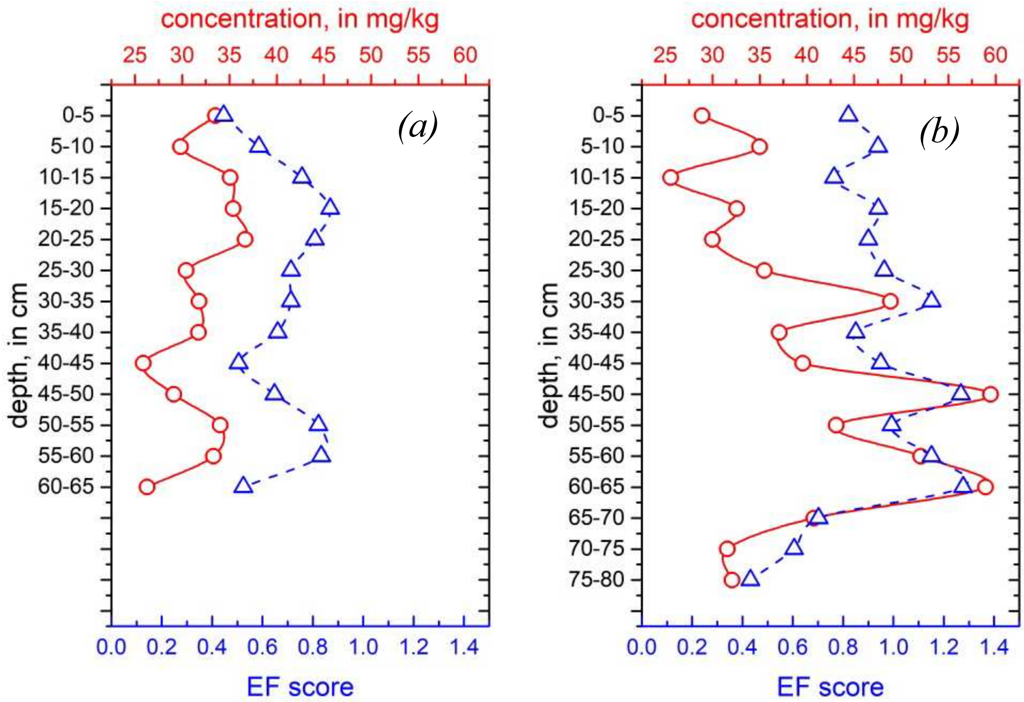

Figure 5. The vertical distribution of Cu (—o—) and EF score for Cu (- -△- -): (a) WFC and (b) EFC in Semarang City.

Vertical distribution of Ni

Ni in both EFC and WFC was also slightly varied and insignificant trend (Figure 6). The unique fluctuation of Ni in WFC occurred at depth 10-50 cm and outside that range the value was around 28-29 mg/Kg. Interestingly, the highest value of Ni happened at depth 40-45 cm co-occurred within the coarser sediment composition) and the lowest Ni was observed during finer sediment composition. In addition, the noticeable value of Ni in EFC was observed only at two depth i.e. highest value at depth 25-30 cm (occurred with increasing coarser sediment composition) and the lowest value at depth 60-65 cm (at decreasing coarser sediment composition).

Uniquely, even it showed an inclination at some depths, sediment was unenriched by Ni as EF score = 0.3-0.7 mg/kg. In contrast, there was two points in EFC as a noticed that Ni input was slightly changes i.e. increased at 25-30 cm (35.2 mg/kg) and decreased at 60-65 cm (24.5 mg/kg). However, that fluctuation has unpolluted the sediment since the no enrichment of Ni was observed (EF score: 0.3-0.5).

Vertical distribution of Pb

Figure 7 showed that vertical distribution of Pb in WFC (5.8-13.4 mg/Kg) was slightly fluctuated compared with Pb in EFC (7.7-22.0 mg/kg). Pb in WFC was slightly varied from top layer to the depth of 40-45 cm then drastically decreased before it was slightly fluctuated again after the depth of 45-50 cm. On the other hand, the drastic fluctuation of Pb in EFC was observed at depth 45 cm downward and the highest Pb was observed at depth 45-50 cm and 60-65 cm. Interestingly, the occurrence of those highest Pb occurred with decreasing coarser sediment composition and vice versa for the lowest Pb in both stations.

In general, the sediment was unenriched by Pb except for in the incline period (depth at 30-40 cm) with EF score= 0.5-1.3. Opposite, Pb in EFC was slightly fluctuated before the depth of 40-45 cm (ranging from 7.95-15.1 mg/kg) then reached its maximum concentration (22.0 mg/kg) before decreased downwards. The upper layer (depth 0-45 cm) implied no significant changes of Pb input and the extreme increase observed after that depth (at depth 45-50 cm). Uniquely, almost all of layers was minor enriched by Pb except during the decline (at depth 10-20 cm, 35-45 cm, 65-70 cm) with EF score = 0.7-2.1.

Vertical distribution of Zn

Figure 8 presented vertical distribution of Zn in both Canal Floods. Slight fluctuation occurred in WFC (74-114 mg/kg) indicated insignificant changes on Zn input. The relatively higher concentration was showed only at the top layer (114 mg/kg) and the depth of 45-50 cm (107 mg/kg). Those highest concentrations of Zn in WFC occurred with increasing coarser sediment composition. In contrast, Zn in EFC was observed at depth 25-30 cm and 45-50 cm matching with the decreasing coarser sediment composition. Thus, the

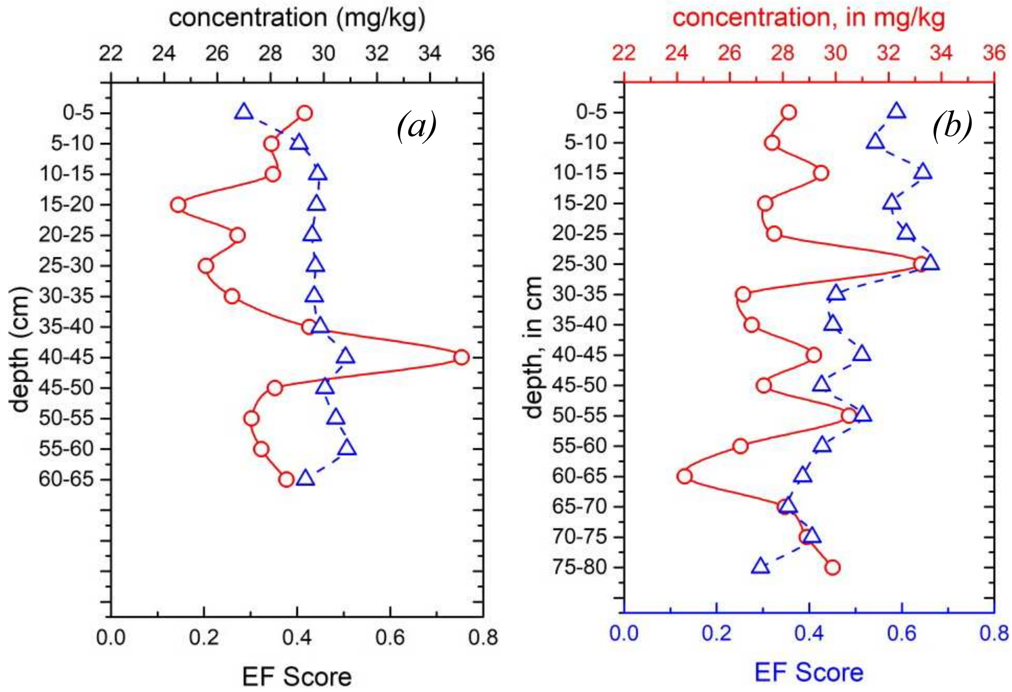

Figure 6. The vertical distribution of Ni (—o—) and EF Score for Ni (- -△-): (a) WFC and (b) EFC in Semarang City.

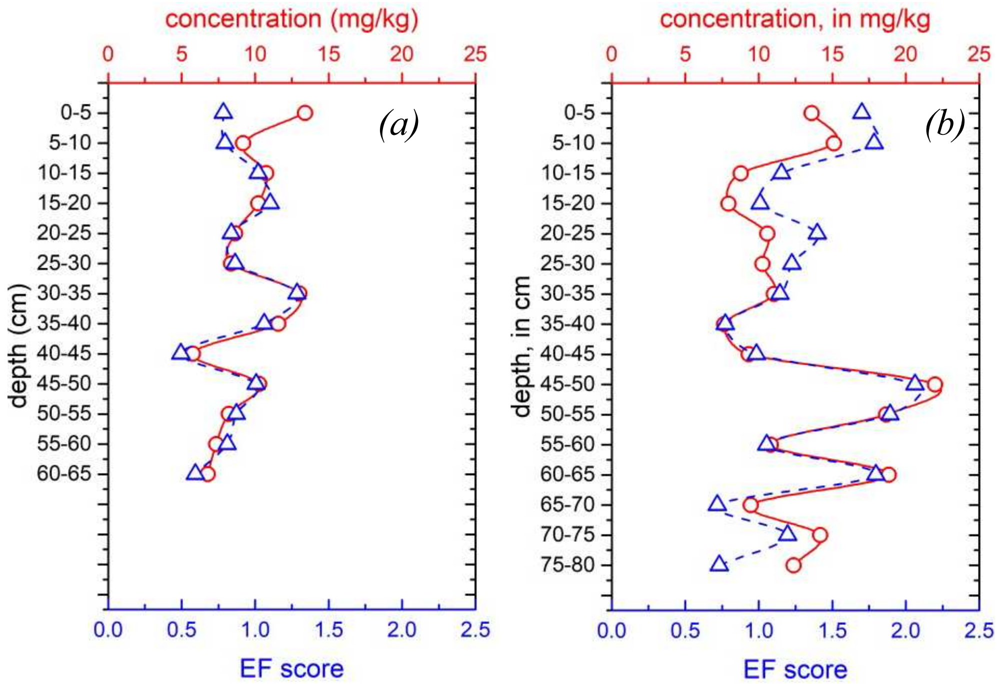

Figure 7. The vertical distribution Pb (—o—) and EF Score for Pb (- -△-): (a) WFC and (b) EFC in Semarang City.

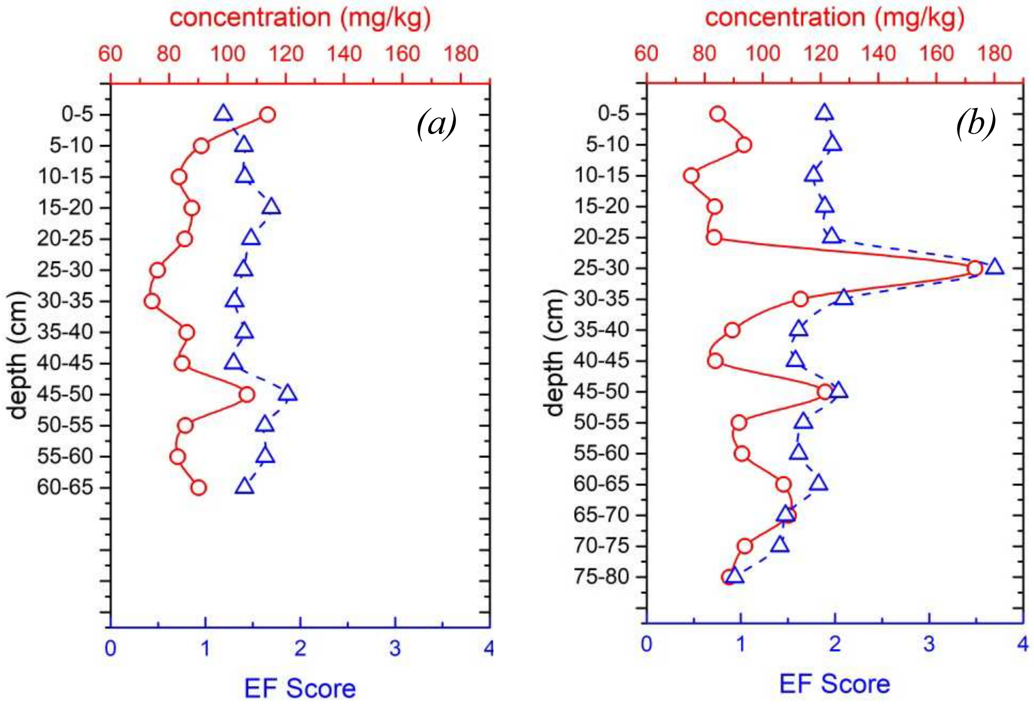

Figure 8. The vertical distribution of Zn (—o—) and EF Score for Zn (- △-): (a) WFC and (b) EFC in Semarang City.

deposition of Zn in EFC occurred in a slow process. Like Pb, Zn in EFC was probably experienced a washing process since it became lower during high energy period.

Uniquely, all layers was minor enriched by Zn with EF score 1.1-1.5 in WFC. In contrast, It was noticed an extreme incline of Zn concentration in EFC. Zn in EFC was slightly fluctuating before the depth of 20-25 cm and no enrichment of Zn occurred (EF<1). Zn reached to its maximum value at the depth of 25-30 cm lead to moderately enrichment then decreased downwards to minor enrichment.

DISCUSSION

It has been shown previously those vertical profiles of the metals in WFC and EFC showed differently, and no consistent correlation between metals and grain size. Commonly, the metal profiles in sediment are related to the environmental deposition and input of metals (Buccolieri *et al.*, 2006; Duquesne *et al.*, 2006 and Sinolungan *et al.*, 2008). This anomaly was very likely stimulated by the difference between two sampling locations in which EFC was located seawards direction making this location to be more exposed to seawater than WFC. Thus, sediment in EFC was more influenced by sea water characteristic and the dynamics within meanwhile WFC was dominantly influenced by freshwater characteristic and riverine discharge.

Generally, each metal investigated in this study illustrated different trend since some of these metals come from different origin. Fe comes from the corrosion of any domestic garbage, steel pipe, steel construction, and fossil fuel (Chatterjee *et al.*, 2007). Even Cd, Cu, Ni, Pb and Zn come from the utilization of fossil fuel, each of them has unique source which may significantly contribute to the high release of this metals in environment. Cd was released by agricultural activities like the use of phosphorous fertilizer (Yu *et al.*, 2013; Helali *et al.*, 2016). The anthropogenic activities releasing Cu comes from fertilizer, thermal power plant, paints and antifouling industries (Suyarso and Susana, 2010; Yu *et al.*, 2013) and untreated waste disposal (Wang *et al.*, 2011). Zn in common pollutant released by human activities such as painting industry, mining and urban life (Yu *et al.*, 2013). In addition, each metal shows different characteristics in sea water and they exhibit different binding capability in sediment like Cd is more stable in dissolved form compared with other metals thus the concentration of this metals in sediment is lower. Therefore, the physicochemical properties like pH, redox potential, and salinity will determine each metal depositional process in sediment (Nemati *et al.*, 2011 and Qiao *et al.*, 2013).

The fluctuation of each metal within these two sediment cores reflected the alteration of their input and their depositional processes. The physical alteration like seasonal monsoon is highly likely affected the processes, for example, in the rainy season more freshwater is discharging for carrying more heavy metals. Thus, by observing the shifting of energy (by the changing of sediment composition), it can be noticed that the higher deposition of Fe, Cd, Cu and Ni in EFC and WFC occurred during higher energy period. That high energy period in both locations are predominantly contributed by high volume of riverine discharge since the location is in the front of river mouth. In addition, anthropogenic activities within Semarang city were also fluctuated. Though, the population was growing in linear rate at a value of 1.8% a year, Suyarso and Susana (2011) reported a fluctuation of industrial growth in both Semarang City and its regency. Their study discovered a stagnant or a slightly decrease of industrial growth at the end of 1998 till beginning of 2005 influencing the metals input to its coastal area. However, the determined data on industrial sector in Semarang city and its regency were not classified each type of industry. That undetailed data produced a difficulty on describing which type of industries and the period of industrial development contributing on environmental degradation along both canals (Suyarso and Susana, 2011).

Interestingly, Cu, Ni, Pb and Zn in both cores were in their natural condition to minor enrichment however Cd in WFC was in moderately enrichment. Though the enrichment was observed, all metals were comparable to other location with noticeable anthropogenic activities. Fe concentration in this study was comparable with Fe from Chilean coastal waters (27230-39860 mg/kg) (Chandía and Salamanca, 2012) and Fe in average earth crust (56300 mg/kg) (Taylor, 1964). Cd in both flood canals in Semarang was relatively higher compared with Changhua River Estuary, Hainan Island (Hu *et al.*, 2013). Cu concentration in both sediment cores was comparable with Cu in sediment from Deception Island, Antarctica (42-65 mg/kg) (Brady *et al.*, 2014) and in Santou Bay, China (48.52 mg/kg) (Qiao *et al.*, 2013). The concentration of Ni along the sediment cores from Semarang Flood Canal was lower than sediment from Izmir Bay, Turkey (73.7 mg/kg) (Kontas, 2007). Pb concentration in both cores was relatively lower than sediment from Shandong Peninsula (Yellow Sea) (19-42.2 mg/kg) (Li *et al.*, 2013). The maximum concentration of Zn observed in this study was higher compared with sediment from Izmir Bay, Turkey (76.7 mg/kg) (Kontas, 2007).

CONCLUSION

Metals in WFC were slightly varied compared with EFC. Generally, the higher Fe, Cd, Cu, Ni, and Zn were observed in coarser-dominated sediment composition yet Pb was co-occurred with finer-dominated sediment composition. Fe concentration in both cores was higher than average metal concentration in continental crust means a massive input in the respective time. Ni in both cores and Cu in WFC were remaining uncontaminated while the rest of studied metals (Cd, Cu in EFC, Pb, and Zn) were fluctuated from unenriched to moderately enriched condition. The fluctuation of metal's concentration along sediment cores reflected the alteration of their input which is could be from the seasonal monsoon/climatic change or industrial development in Semarang city and regency.

ACKNOWLEDGEMENT

The research was funded by DIPA TEMATIK of Research Center for Oceanography-LIPI year of 2016. The authors are also conveying our sincere gratitude for all laboratory assistants i.e. Mr. Abdul Rozak, Mr. Taufik Kaisupy and Mr. Singgih Prasetyo Adi Wibowo for the precious assistance in the laboratory.

REFERENCES

Argese, E., Cogoni, G., Zaggia, L., Zonta, R., and Pini, R., 1992. Study on Redox State and Grain Size of Sediments in a Mud Flat of the Venice Lagoon. *Environmental Geology and Water Sciences*, 20 (1): 35-42. doi:10.1007/BF01736108.

Bingöl, D., Ay, Ü., Bozbas, S.K. and Uzgören, N. 2013. Chemometric evaluation of the heavy metals distribution in waters from the Dilovas region in Kocaeli, Turkey. Marine pollution bulletin, 68 (1-2): 134-139.

Brady, J.P, Ayoko, G,, Martens, W.N., and Goonetilleke, A., 2014. Enrichment, Distribution and Sources of Heavy Metals in the Sediments of Deception Bay, Queensland, Australia. *Marine Pollution Bulletin*, 81 (1): 248–255. doi:10.1016/j.marpolbul.2014.01.031.

Buccolieri, A., Buccolieri, G., Cardellicchio, N., Antonella, A.D., Leo, D., and Maci, A., 2006. Heavy Metals in Marine Sediments of Taranto Gulf (Ionian Sea, Southern Italy). *Marine Chemistry*, 99 (1–4): 227–235. doi:10.1016/j.marchem.2005.09.009.

Chakraborty, P., Ramteke, D., Chakraborty, S., and Nath, B.N., 2014. Changes in Metal Contamination Levels in Estuarine Sediments around India--an Assessment. *Marine Pollution*

Bulletin, 78 (1–2): 15–25. doi:10.1016/ j.marpolbul.2013.09.044.

Chandía, C., and Salamanca, M., 2012. Long-Term Monitoring of Heavy Metals in Chilean Coastal Sediments in the Eastern South Pacific Ocean. *Marine Pollution Bulletin*, 64 (10): 2254–2260. doi:10.1016/j.marpolbul.2012.06.030.

Chatterjee, M., Silva Filho, E. V., Sarkar, S. K., Sella, S. M., Bhattacharya, A., Satpathy, K. K., Prasad, M. V. R., Chakraborty, S., and Bhattacharya, B. D., 2007. Distribution and Possible Source of Trace Elements in the Sediment Cores of a Tropical Macrotidal Estuary and Their Ecotoxicological Significance. *Environment International*, 33 (3): 346–356. doi:10.1016/j.envint.2006.11.013.

Duquesne, S., Lyn, C. N., Lorenzo, G., Susan, B. M., Stärk, H.-J., and David, J. B., 2006. Evidence for Declining Levels of Heavy-Metals in the Severn Estuary and Bristol Channel, U.K. and Their Spatial Distribution in Sediments. *Environmental Pollution*, 143 (2): 187–196. doi:10.1016/j.envpol.2005.12.002.

El-Said, G.F., Draz, S.E.O., El-Sadaawy, M.M., and Moneer, A.A., 2014. Sedimentology, geochemistry, pollution status and ecological risk assessment of some heavy metals in surficial sediments of an Egyptian lagoon connecting to the Mediterranean Sea. *Journal of Environmental Science and Health*, 49:1029-1044.

Helali, M.A., Oueslati, W., Zaaboub, N., Added, A., and Aleya, L., 2016. Chemical Speciation of Fe , Mn , Pb , Zn , Cd , Cu , Co , Ni and Cr in the Suspended Particulate Matter off the Mejerda River Delta (Gulf of Tunis, Tunisia). *Journal of African Earth Sciences*, 118: 35–44. doi:10.1016/j.jafrearsci.2016.02.013.

Hu, B., Cui, R., Li, J., Wei, H., Zhao, J., Bai, F., Song, W., and Ding, X., 2013. Occurrence and Distribution of Heavy Metals in Surface Sediments of the Changhua River Estuary and Adjacent Shelf (Hainan Island). *Marine Pollution Bulletin*, 76 (1–2): 400–405. doi:10.1016/j.marpolbul.2013.08.020.

Huang, K-M, and Lin, S., 2003. Consequences and Implication of Heavy Metal Spatial Variations in Sediments of the Keelung River Drainage Basin, Taiwan. *Chemosphere*, 53 (9): 1113–1121. doi:10.1016/S0045-6535(03)00592-7.

Hutton, M., 1983. Sources of Cadmium in the Environment. *Ecology and Environmental Safety*, 7(1): 9-24. doi:10.1016/0147-6513(83)90044-1.

Kontas, A., 2007. Trace Metals (Cu, Mn, Ni, Zn, Fe) Contamination in Marine Sediment and Zooplankton Samples from Izmir Bay. (Aegean Sea, Turkey). *Water, Air, and Soil Pollution*, 188 (1–4): 323–333. doi:10.1007/s11270-007-9547-1.

Li, G., Hu, B., Bi, J., Leng, Q., Xiao, C., and Yang, Z., 2013. Heavy Metals Distribution and Contamination in Surface Sediments of the Coastal Shandong Peninsula (Yellow Sea). *Marine Pollution Bulletin,* 76 (1-2): 420-426. doi:10.1016/j.marpolbul.2013.08.032.

Loring, D.H., and Rantala, R.T.T., 1992. Manual for the Geochemical Analyses of Marine Sediments and Suspended Particulate Matter. *Earth-Science Reviews*, 32 (4): 235–283. doi:10.1016/ 0012-8252(92)90001-A.

Morita, Y., Yamagata, K., Oota, A., Ooki, A., Isoda, Y., and Kuma, K., 2017. Subarctic Wintertime Dissolved Iron Speciation Driven by Thermal Constrain on Fe(II) Oxidation, Dissolved Organic Matter and Stream Reach. *Geochimica et Cosmochimica Acta*, 215: 33-50. doi:10.1016/j.gca.2017.07.009.

Mukherjee, D P. 2014. Dynamics of Metal Ions in Suspended Sediments in Hugli Estuary, India and Its Importance towards Sustainable Monitoring Program. *Journal of Hydrology*, 517 (0): 762–776. doi:http://dx.doi.org/10.1016/ j.jhydrol.2014.05.069.

Nemati, K., Bakar, N.K.A., Abas, M.R., and Sobhanzadeh, E., 2011. Speciation of Heavy Metals by Modified BCR Sequential Extraction Procedure in Different Depths of Sediments from Sungai Buloh, Selangor, Malaysia. *Journal of Hazardous Materials*, 192 (1): 402–410. doi:10.1016/j.jhazmat.2011.05.039.

Pekey, H., 2006. The Distribution and Sources of Heavy Metals in Izmit Bay Surface Sediments Affected by a Polluted Stream. *Marine Pollution Bulletin*, 52 (10): 1197–1208. doi:10.1016/j.marpolbul.2006.02.012.

Qiao, Y., Yang Y., Gu, J., and Zhao. J., 2013. Distribution and Geochemical Speciation of Heavy Metals in Sediments from Coastal Area Suffered Rapid Urbanization, a Case Study of Shantou Bay, China. *Marine Pollution Bulletin*, 68 (1–2): 140–146. doi:10.1016/ j.marpolbul.2012.12.003.

Raize, O., Argaman, Y., and Yannai, S.. 2004. Mechanisms of Biosorption of Different Heavy Metals by Brown Marine Macroalgae. *Biotechnology and Bioengineering*, 87 (4): 451–458. doi:10.1002/bit.20136.

Ribeiro, J. Sabadini-Santos, E., Carvalho, C., Annes, K.,César, R., and Bidone, E.D., 2017. Bioaccumulation of Heavy Metals by Shrimp (Litopenaeus Schmitti): A Dose – Response Approach for Coastal Resources Management. *Marine Pollution Bulletin*, 114 (2): 1007–1013. doi:10.1016/j.marpolbul.2016.11.013.

Sakellari, A., Plavši , M., Karavoltsos, S., Dassenakis, M., and Scoullos, M., 2011. Assessment of Copper, Cadmium and Zinc Remobilization in Mediterranean Marine Coastal Sediments. *Estuarine, Coastal and Shelf Science,* 91 (1): 1–12. doi:10.1016/j.ecss.2010.09.008.

Sinolungan, M., T. M., Soeroto, B., Kondo, F., and Koumoto, T., 2008. The Geochemical Characteristics of Sediment in Tondano Lake, Indonesia: Heavy Metals and Organic Matter Contents, and Grain Size Distribution. *Paddy and Water Environment*, 6 (3): 341–348. doi:10.1007/s10333-008-0132-z.

Suyarso and Susana, T., 2010. Preliminary study on evolution of metals contaminant recorded in the coastal sediments of Semarang watres. *Journal of Coastal Development*, 13 (3): 185-194.

Taylor, S.R. 1964. Abundance of Chemical Elements in the Continental Crust?: A New Table. *Geochimica et Cosmochimica Acta*, 28: 1273–1285.

Thévenot, D.R, Moilleron, R., Lestel, L., Gromaire, M., Rocher, V., Cambier, P., Bonté, P., Colin, J-L., de Pontevès, C., and Meybeck. M., 2007. Critical Budget of Metal Sources and Pathways in the Seine River Basin (1994-2003) for Cd, Cr, Cu, Hg, Ni, Pb and Zn. *The Science of the Total Environment*, 375 (1–3): 180–203. doi:10.1016/j.scitotenv.2006.12.008.

Wang, M., Bai, Y., Chen, W., Markert, B., Peng, C., and Ouyang, Z., 2012. A GIS Technology Based Potential Eco-Risk Assessment of Metals in Urban Soils in Beijing, China. *Environmental Pollution*, 161 235–242. doi:10.1016/ j.envpol.2011.09.030.

Wang, Y., Yang, Z., Shen, Z., Tang, Z., Niu, J., and Gao, F., 2011. Assessment of Heavy Metals in Sediments from a Typical Catchment of the Yangtze River, China. *Environmental Monitoring and Assessment*, 172 (1–4): 407–417. doi:10.1007/s10661-010-1343-5.

Wentworth, C.K., 1922. A scale of grade and class terms for clastic. *The Journal of Geology*, 30: 377-392.

Yu, Y., Song, J., Li, X.,Yuan, H., and Li. N., 2013. Fractionation, Sources and Budgets of Potential Harmful Elements in Surface Sediments of the East China Sea. *Marine Pollution Bulletin*, 68 (1–2): 157–167. doi:10.1016/ j.marpolbul.2012.11.043.

Zhang, P. Hu, R., Zhu, L., Wang, P.,Yin, D., and Zhang, L. 2017. Distributions and Contamination Assessment of Heavy Metals in the Surface Sediments of Western Laizhou Bay?: Implications for the Sources and in Fl Uencing Factors. *Marine Pollution Bulletin*, 119 (1): 429–438. doi:10.1016/ j.marpolbul.2017.03.046.

Zorer, Ö. S., Ceylan, H., and Do ru, M., 2008. Determination of Heavy Metals and Comparison to Gross Radioactivity Concentration in Soil and Sediment Samples of the Bendimahi River Basin (Van, Turkey). Water, Air, and Soil Pollution, 196 (1–4): 75–87. doi:10.1007/s11270-008-9758-0.