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Full Length Research Paper

Temporal and spatial variations of heavy metals (Cu, Pb and Ni) concentration in the sediment from intertidal zone along the Iranian coasts of the Oman Sea

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In order to determine distribution and seasonal patterns of heavy metals concentration in the intertidal sediment of the north Oman sea, samples of sediment were collected from five different station in August 2007 and February 2008. The samples were oven dried and acid digested. Heavy metals content of acid digested samples were analyzed by atomic absorption spectrophotometery method. Results showed that mean Cu, Pb and Ni concentration during summer were 38.28 ± 0.37, 50.37 ± 2.41 and 26.90 ± 2.72 µg.g^{-1} respectively. The average heavy metals concentration in winter was sharply dropped to 16.45 ± 1.77, 13.56 ± 1.24 and 14.68 ± 1.93 µg.g^{-1} for Cu, Pb and Ni respectively. Though Cu and Ni concentration did not significantly change over various station, seasonal difference between heavy metals concentration in sediment was significant ($P < 0.05$). It is suggested that Cu and Ni originate from non point sources. The heavy metals concentration in the sediment may hardly be affected by monsoon.

Key words: Heavy metals, intertidal zone, sediment.

INTRODUCTION

Marine environment particularly intertidal zone is very complicated natural system, since it is affected by many processes including human activities (Qiao et al., 2007; Pote et al., 2008), physicochemical and biological processes (Fulton et al., 2004; Gonza´lez-Mac´ias et al., 2006) and even atmospheric depositions (Witt et al., 2010). Human activities in the coastal area always result in production and discharge of various kinds of pollutants such as heavy metals into the marine ecosystems (Censi et al., 2006).

Heavy metals are normally present in marine environment at low concentration (Karuppiah and Obbard, 2008; Garc´ıa et al., 2001; Kim et al., 2003; Santos et al., 2005; Catsiki and Florou, 2006; Nobi et al., 2010), however, considerable amount of them are released to the marine ecosystems from anthropogenic sources (Kamala-Kannan et al., 2008). These heavy metals may settle or accumulate in the coastal area apparently due to their affinity to be bounded to particulate organic matter and deposition in marine sediment (Tam and Wong, 2000; Santos et al., 2005; Mil-Homens et al., 2007; El Nemr et al., 2007). Heavy metals are considered as persistent contaminants and due to their toxic properties, the elevated levels of them in aquatic systems could create several problems for marine organisms. Moreover their accumulations in marine organisms and biomagnification throughout the food chain may affect human health (Kowalski, 1994; Valls and Lorenzo, 2002; Gochfeld, 2003; Yi et al., 2008).

The accumulation, biomagnification and toxic behaviors of heavy metals in the marine environment is greatly influenced by their bioavailability, which in turn depends on many factors such as nature of sediment, environmental conditions including pH, temperature, redox potential, water turbulence and properties of the absorbed compounds (Tam and Wong, 2000; Santos et

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al., 2005; Mil-Homens et al., 2007; El Nemr et al., 2007). Normally sediment act as a marine sink for discharged heavy metals into the marine environment (Di Tao et al., 1992; Morillo et al., 2004; Wang et al., 2004; IP et al., 2007). Meanwhile deposited metals in the sediment may return to the water column again as a result of bottom turbulence created by strong waves (Simpson and Batley, 2007; Alagarsamy, 2006; Anu et al., 2010). Infact coastal sediments have been widely used to evaluate sea water quality because, it has more stability and less variability of heavy metals concentration compared to the sea water (RuiźFernández et al., 2003; Cuong and Obbard, 2006). In some circumstances, information about the concentration of heavy metals in sediment can help to detect the source of pollution in the aquatic ecosystems (Birch et al., 2001; Liu et al., 2003; Alagarsamy, 2006; Silva et al., 2006).

Located at Iranian coasts of the Oman Sea, Chabahar is a developing area. Traditionally this area is used for fisheries and aquaculture activities of the local people. However it has developed as an important free zone for country import and export, economy, urbanization and industries have also grown in the area parallel to economic development (Amini and Miraki, 2006). This area has a subtropical weather with two distinct seasons, dry season in summer and rainy season in winter. It also experience monsoon (seasonal western winds) during summer and winter. The sea water is completely disturbed by huge waves during monsoon period (Zareii, 1995). Therefore considerable amount of sediment is displaced by the power of waves. This condition could result in redistribution of heavy metals in the coastal environment. Although the area is still growing and especial weather seems to greatly influence on distribution and redistribution of heavy metals in coastal ecosystems, there is a lack of information concerning heavy metals contamination in Chabahar. Such information could be used to establish baselines in the area. The Study of De Mora et al (2004) in southern coasts of the Oman Sea showed, some metals like the Ni have natural source in this area. Mainwhile, the human activity including shipping, fishing activity and cannery industry can increase the Pb concentration in coastal area. These activity are conducted in Iranian coasts of the Oman Sea. These metals also can be accumulated in tissues of organisms (Gochfeld, 2003; Yi et al., 2008). Therefore, the objective of this study was to investigate Cu, Pb and Ni concentration in sediment of northern coasts of the Oman Sea and determine the seasonal variation of these metals in this area.

MATERIALS AND METHODS

Study area

Sediment samples were taken from five different locations (including Guatr bay, Beriss, Ramin, Shahid Beheshti and Chabahar bay) along intertidal zone of the north coasts of the Oman Sea in February 2007 and August 2008 (Figure1). Geographical position of the sampling station and current sources of metals input are shown in Table 1.

Sample collection and preparation

From each location, three sediment samples were taken from 3 to 5 cm surface with a stainless steel grab sampler during low tide. Samples were collected in acid washed polyethylene bottles and transferred to the laboratory with icebox. Each sample was mixed thoroughly and dried at 105°C in drying oven for at least 16 h until a constant weight was obtained (Delman et al., 2006). Dry samples were sieved with 63 µm stainless steel seive to remove shells and other debrises, were powdered in a glass mortar, stored in plastic container which were acid washed in 10% solution of nitric acid, rinsed with double distillated water and preserved for the determination of heavy metal concentration (Delman et al., 2006; Orescanin et al., 2006).

Sample analysis

For analysis of heavy metals in sediment of each station, 1 g of each dry sample was digested in a mixture of 10 cc concentrated perchloric acid (60% Merck) and Nitric acid (65%Merck) in the 1:4 ratio with hotplate digester first at 40°C for 1h and then in 140^0C for 3h. After digestion, the samples were cooled in laboratory temperature, diluted to certain volume using double distilled water and then filtered by Whattman 42 µ filter paper (Delman et al., 2006; Yap et al., 2002). Heavy metal concentration including Cu, Pb and Ni were measured using Unicam 919 air-acetylene atomic absorption spectrophotometer and detailed measurements of each metal is listed in the Table 2. The metals concentration were measured and expressed as microgram per gram in dry weight (µg/g dw).

Data analysis

All data were tested for normal distribution first. The normality test revealed all data were normally distributed. In order to compare differences between seasonal variation of heavy metal concentration t-test analysis was used. One-way analysis of variance (ANOVA) was used to find any significant difference in metal concentration among different station. If significant difference was observed, Tukey post hoc test was employed to determine different station.

RESULTS

The overall pattern of heavy metals concentration in the sediment was Pb > Cu > Ni. Copper concentration in the sediment of various sampling station were not significantly different (P > 0.05) either in Summer or Winter. The concentration of Cu in Summer was 38.47 ± 1.00, 38.69 ± 0.62, 37.88 ± 0.70, 38.07 ± 0.10 and 38.29 ± 0.15 g/g dw for Guatr, Beriss, Ramin, Shahid Beheshti and Tiss respectively. A sharp decrease in Cu concentration was appeared in Winter. During this season the level of Cu was 16.23 ± 1.88, 16.96 ± 2.26, 16.96 ± 2.26, 15.87 ± 1.25 and 16.25 ± 1.21 g/g dw for

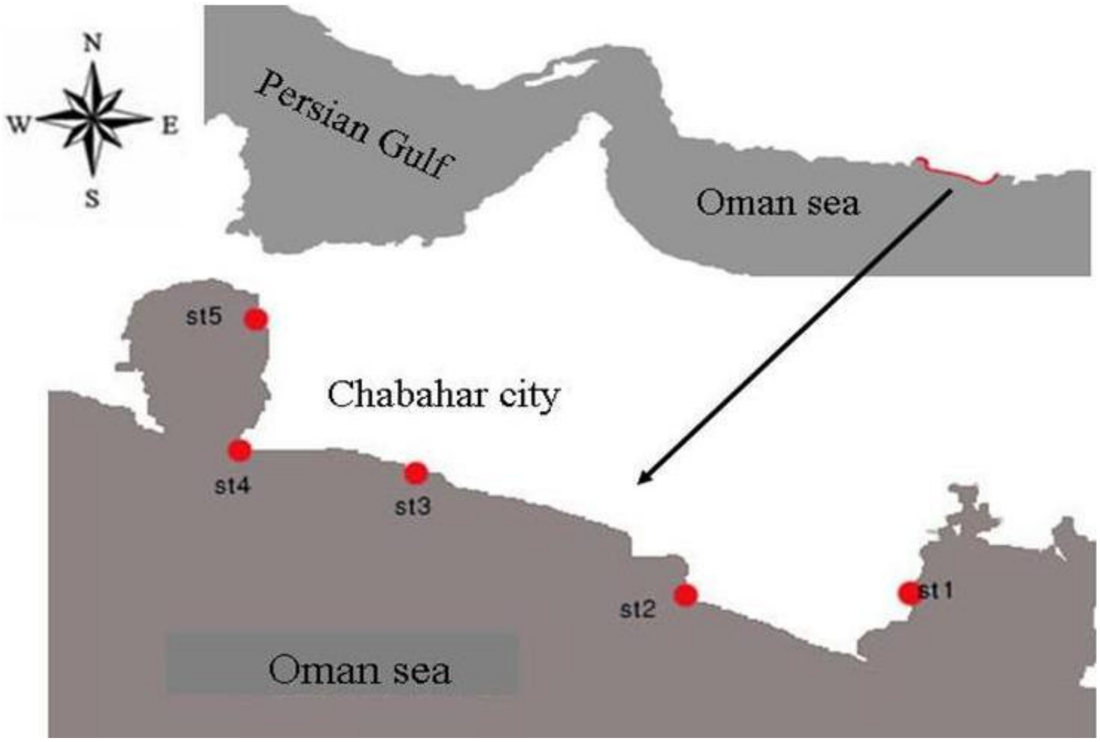

Figure 1. Map showing study area.

Table 1. Position of stations along Chabahar coasts.

Sources of heavy metal input	Latitudes	Station	
Aquaculture and Fishing boats	″ 3/9 ' 30 °61 E ″1/53 '9 25 N	Guatr	St1
Port, transportation, food industries, aquaculture, domestic discharges	" 6/5 ′ 10.3 °61 E "55/7 '8 °25 N	Beriss	St2
Port, transportation, food industries, aquaculture, domestic discharges	″50 '44 °60 E ″3/9 ′16 °25 N	Ramin	St3
Domestic discharges, Port and transportation	″ 7/12 ' 37 °60 E ″ 92/9 ' 21 °25 N	Shahid Beheshti	St4
Agriculture, aquaculture, domestic discharges	" 5/21 ′ 37 °60 E " 2/39 ′ 17 °25 N	Tiss	St5

Guatr, Beriss, Ramin, Shahid Beheshti and Tiss respectively. The Cu content of the sediment in August and February were significantly different (Figure 2).

Comparison between Pb concentration in the sediment showed significant difference among different station. The maximum concentration of Pb was recorded in Ramin (56.45 g/g dw) during summer. On the other hand, Beriss was characterized by significantly higher Pb concentration among other studied station in winter ($P < 0.05$). While, during summer Pb concentration was measured as 50.25 ± 1.53, 44.93 ± 2.65, 56.45 ± 4.06, 48.48 ± 4.60 and 51.78 ± 3.27 g/g dw for Guatr, Beriss, Ramin, Shahid Beheshti and Tiss respectively. A significant decrease was observed in Pb level during Winter ($P < 0.05$). It was measured as 13.33 ± 1.29, 15.79 ± 1.52, 15.61 ± 1.90, 12.09 ± 0.35, and 10.98 ± 1.14 g/g dw for Guatr, Berris, Ramin, Shahid Beheshti and Tiss in February (Figure 3).

Table 2. The details of atomic absorptaion spectrophotometer Unicam 919 for each metal.

Metal	Wavelength (MA)	Lump current (Cathodic lump) (NM)	Band width (NM)	Fuel
Cu	324	3.5	0.5	Acetylene gas
Pb	216.2	5	1	Acetylene gas
Ni	224	3.5	0.2	Acetylene gas

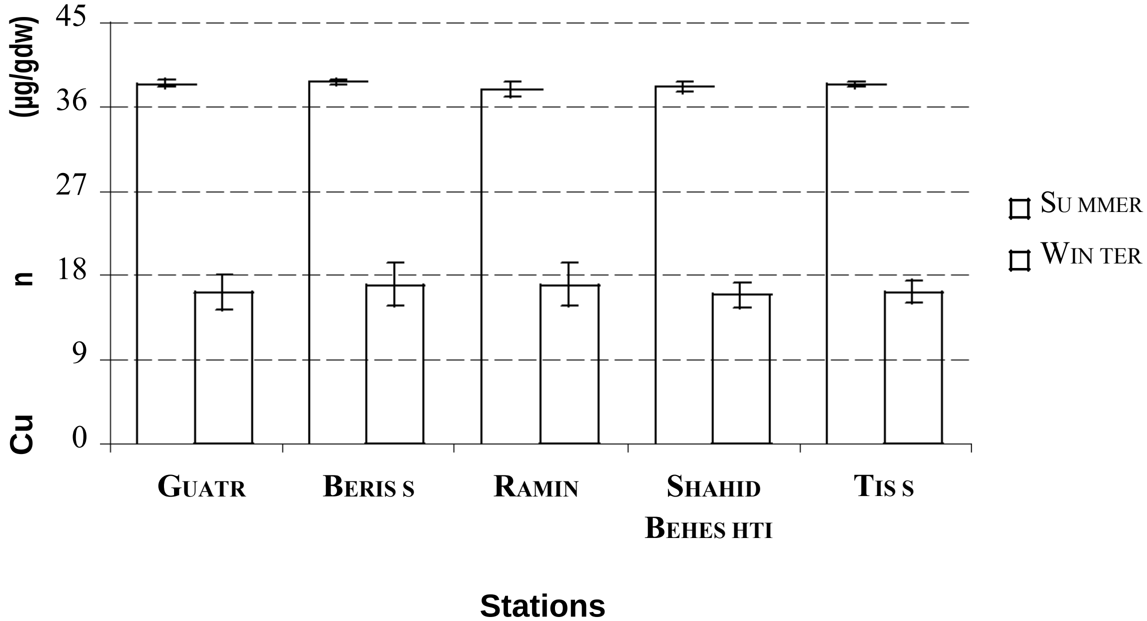

Figure 2. Cu concentrations (g/g dw) in sediment in summer and winter.

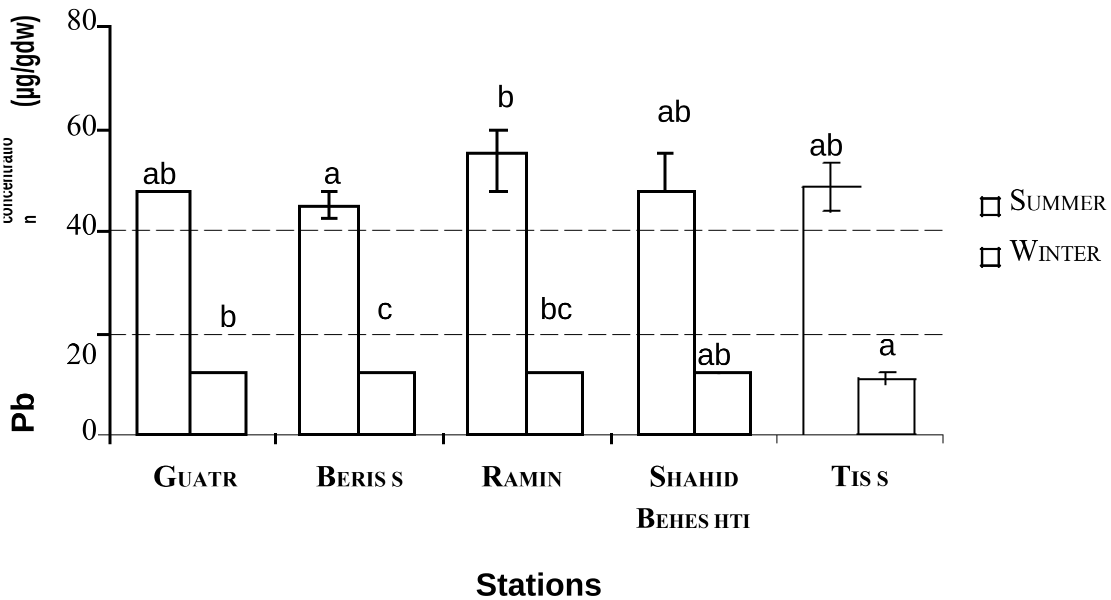

Figure 3. Pb concentrations (g/g dw) in sediment in summer and winter.

The level of Ni in the sediment did not vary significantly among different station either in August or February.

During Summer Ni concentration in the sediment was 25.69 ± 2.22, 30.28 ± 2.40, 28.42 ± 2.54, 26.41 ± 5.42

and 23.74 ± 1.06 g/g dw for Guatr, Beriss, Ramin, Shahid Beheshti and Tiss respectively. As for other metal again significant decrease was found in Ni concentration in February. During Winter Ni level dropped to 12.39 ± 1.86, 17.10 ± 1.78, 14.46 ± 2.33, 13.55 ± 0.98 and 15.91 ± 2.71 g/g dw in station Guatr, Beriss, Ramin, Shahid Beheshti and Tiss respectively (Figure 4).

DISCUSSION

The maximum concentration of Pb was observed in Ramin during summer and in Beriss during winter. Elevated Pb concentration in mentioned station, could be related to human activities in these locations. Intense marine transportation, ship painting, fishing boats activities, aquaculture, polluted wastes and discharges from residential area could be the major factors for Pb input in these station. Another factor which could be involved in Pb input in Ramin and Beriss station is adjacent mountains. The distance between mountains and sea is minimum in these station compared to others. Therefore weathering of the lead containing rocks may increase the level of Pb in coastal sediment. Kilemade et al. (2004) suggested that short distance between mountains and coasts can be an important factor to increase the concentration of heavy metals in the marine environment.

Zhou and Hao (2007) suggested that anthropogenic sources including antifouling paint, domestic sewage, surface runoff, wastewater, vehicle emissions, marine transportation, ship repainting, dental clinics, electronic/ chemical industries and rock weathering sea could be important factors affecting metals concentration in the coastal sediments of Hong Kong.

Despite the existence of the wastes in station Beriss, the concentration of Pb measured in this station during summer was low. This could be related to high disturbance of the sediment created by huge waves during monsoon. In fact during monsoon season, sea water in Beriss is so disturbed and wavy that most local activities including shipping and fishing stop in some locations (Zareii, 1995). Subsequently, after this reduction of human activities, the level of Pb input by the local vessels might be decreased leading to occurrence of low Pb concentration in sediment. After monsoon, by the starting of local activities, Pb input starts to increase due to the beginning of local shipping and human activities in the area. The sediment is more stable, leading Pb level to rise up again.

The concentration of Cu and Ni did not changed significantly in studied station ($P > 0.05$). Both in summer and winter it is suggested that Cu and Ni mainly originate from natural sources. Geological studies of the Oman Sea have revealed that the sea bed is reach in Ophiolits. This mineral contains considerable amounts of Nickel sulphide (Leblanc and Ceuleneer, 1991). Therefore, it seems that the more or less constant concentration of Ni in different station in much influenced by local mineralogy derived from Oman ophiolites than anthropogenic input. De Mora et al. (2004) found high concentration of Ni and Cr in sediment from Akkah in southern coasts of the Oman Sea where located is far from sever human activities and anthropogenic inputs. They also suggested that Nickel sulphide rich Ophiolits are the main sources of Ni found in the sediment.

Comparisons between heavy metals content of sediment in summer and winter indicated that all metals concentration were higher in summer (August). Increasing of human activities such as shipping and transportation together with enhanced growth of phytoplankton in the water column due to upwelling and nutrient availability and favorite environmental factors (temperature) during monsoon, are suggested to be the main factors. Increasing of human activities may result in elevated Pb input, while the occurrence of high phytoplankton growth in the water column promotes the production of higher amounts of suspended organic matter. These materials have affinity to bound with metal ions which are dissolved in seawater. The complex particles finally deposit on the bottom sediment and increase the metals concentration. In addition, seasonal variation of is also depend on the availability of other metals and compounds in the same site which may bind or unbind the presently studied metals, so it is not totally depended on the anthropogenic studies. Seasonal growth of phytoplankton may also influence the concentration of heavy metals.

Similar to present results, Lee et al. (2008) found that heavy metals concentration in the sediment of the South Korean coasts had increased during summer. They suggested that optimization of physicochemical factors of seawater (ie. dissolved oxygen, temperature and pH) during spring may stimulate phytoplankton growth which finally in turn results in appearance of algal blooms. The production of great amounts of organic carbon in sea water due to phytoplankton growth and chelation of dissolved metals and settlement of the chelated metals increase heavy metal concentration in the sediment (Lee et al., 2008). Like phytoplankton macrophytes can also affect heavy metals concentration in the sediment by the same way. Rigollet et al. (2004) concluded that when organic production by Zostrea is low, heavy metals were found at lower concentration in sediment while, after a period of Zostrea growth at the end of summer heavy metals concentration in sediment rose up.

Conclusion

The Level of Cu and Ni did not significantly change among different station suggesting that these two elements originate from natural sources. The concentration of Pb varied among different station with maximum

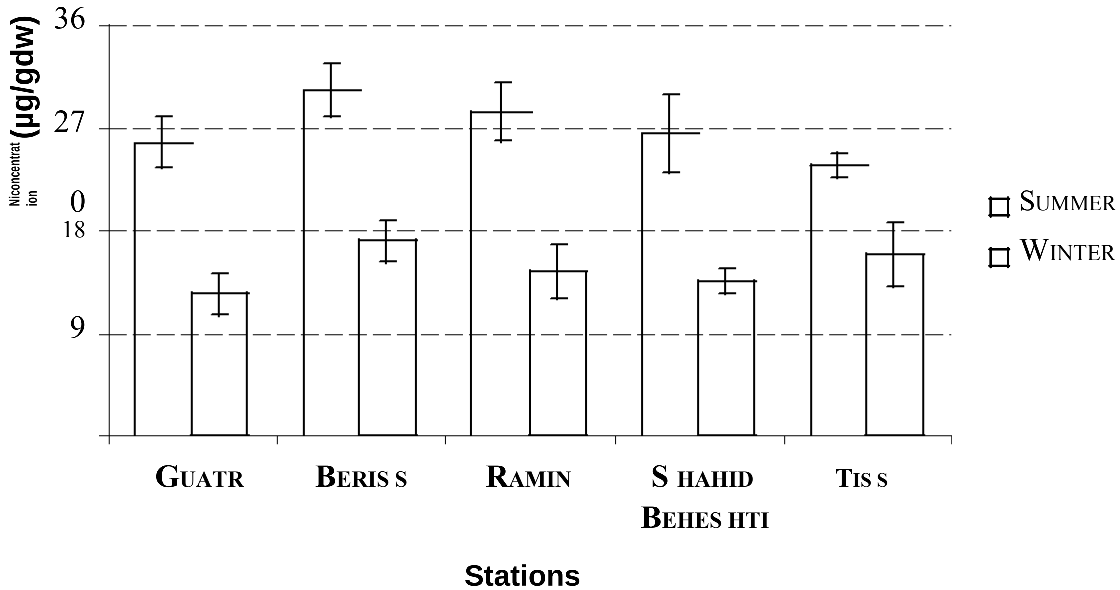

Figure 4. Ni concentrations (g/g dw) in sediment in summer and winter.

levels in Beriss and Ramin. Human activities such as shipping, marine transportation and fisheries are might associate in heavy metals enrichment in the sediment. During summer heavy metals concentration in Chabahar sediment increased markedly. It is suggested that increasing of nutrient availability due to upwelling during monsoon season (summer) enhanced phytoplankton growth followed by increasing of suspended organic matter which should be involved in heavy metals enrichment of sediment. So can the variation in heavy metals concentration be correlated to the evaporation rate of water during the winter and summer. To understand the exact effect of monsoon on heavy metal concentration in the sediment more detailed study is recommended.

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