BioTechnology

An Indian Journal

FULL PAPER

Assessment of metal contamination using pollution indices in surface sediments from Dongzhai harbor (Hainan Island)

Jie Yang[1,2], Junjie Zhou[1], Zhihang Li[1], Chuguang Huang[1],
Weixu Cai[1,*], Hongda Fang[1]
[1]South China Sea Marine Environment Monitoring Center, SOA, Guangzhou
Guangdong, 510915, (P.R.CHINA)
[2]School of Earth Sciences and Engineering Geology, Guangdong Provincial Key
Laboratory of Geological Processes and Mineral Resource Exploration, Sun Yat-Sen
University, Guangzhou Guangdong, 510275, (P.R.CHINA)
E-mail : caiwx@163.com

ABSTRACT

Selected heavy metals (Cu, Zn, Pb, Cd, As) in surface sediments from Dongzhai Harbor, Hainan Island in May 2010, have been determined to evaluate the metal contamination and potential ecological risk using pollution indices. Results showed that As may occur occasional biological effect by numerical Sediment Quality Guidelines. Further, Geoaccumulation indices (I_{geo}) suggest there are serious pollution levels of As at all five stations. However, Spatial distribution of ecotoxicological index suggested that most of the surface sediments have a 9% probability of being toxic. Similar results were also obtained by pollution load index. the pollution load index(PLI) revealed that the potential ecological risk zone appear in northern and southern of Dongzhai Harbor. Multivariate analysis indicated that most of the metals primarily originate from natural sources. As and Pb resulted primarily from aquaculture, and combustion of gasoline and diesel fuel by ships. The present study provides a baseline record of heavy metals in mangrove surface sediments on the Dongzhai Harbor, and provide a useful aid for sustainable marine management in this region.

KEYWORDS

Heavy metal; Sediment; Risk assessment; Dongzhai harbor; Hainan island.

INTRODUCTION

Heavy metal contamination in aquatic environment has drawn particular attentions due to their toxicity, persistence and biological accumulation[1]. Heavy metals have low solubility and primarily get absorbed and accumulated on bottom sediments. Bottom marine sediments are sensitive indicators for monitoring pollutants as they act as a sink and a carrier for contaminations in aquatic environment[2]. The study of bottom bay sediments plays an important role for their longer residence time, and the role is called "the record of history"[3]. Thus, spatial surveys of metal concentrations in the sediments are useful to assess pollution in the marine environment and to provide basic information for the judgment of environmental health risks.

The Mangrove ecosystems are unique coastal estuarine systems confined to the tropical and subtropical regions[4]. These zones are dominated by mangrove plants, which are highly productive and play a vital role, both as the major primary producers in estuarine ecosystems and meanwhile, it is the most endangered one[5]. Mangrove becomes the source and collection area of heavy metals usually, belonging to the connection of ocean and land[6]. Therefore, mangrove ecosystem is recently a topic of much discussion. Mangrove of Dongzhai Harbor in Hainan is a national important mangrove ecosystem protection area. In this region, there are lots of works about heavy metal distribution. However, no detailed study has so far been conducted especially on ecological risk assessment for heavy metals contamination in depositional environment. Therefore, the present investigation aimed to study the levels of metals (Cu, Zn, Pb, Cd, As) in sediment samples of Dongzhai Harbor, primarily to generate data on evaluate the degree of contamination and potential ecological risk and offer some theoretical significance and practical value for mangrove ecosystem protection.
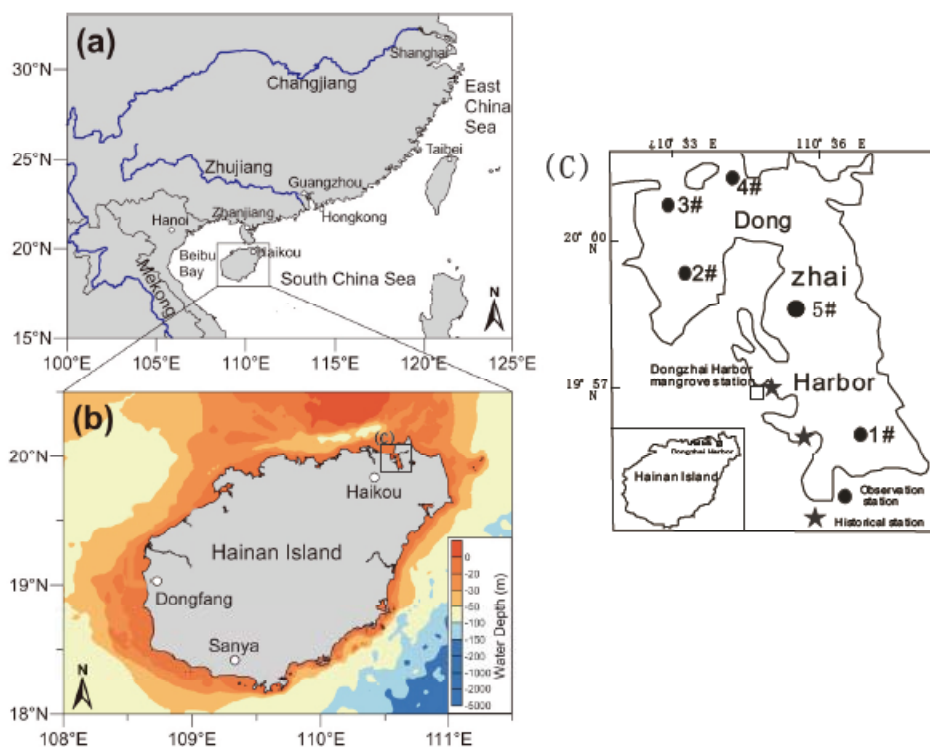
Figure 1 : Map of sampling stations

MATERIALS AND METHODS

A total of 5 surface sediment (0-5 cm) samples were collected by a grab sampler using a small vessel in July 2010 (Figure 1). All samples were stored in refrigerators at 4℃ until analysis. All samples were oven-dried at 45 ℃ for 24 h. After removing the gravels and large debris, about 20 g of the subsamples were ground with agate mortar and pestle, and then to pass a 0.125 mm sieve and stored in clean plastic bags at room temperature prior to analyses. The concentrations of Cu, Pb, Zn, Cd and As were all detected by means of inductively coupled plasma-mass spectrometry (ICP-MAS). Blanks and China Stream Sediment Reference Materials (GBW07345, GSD9, and GSD4) were included in the analyses for data QA/QC. Replicated samples were measured with a variation of <10%.

RESULTS AND DISCUSSION

As shown in TABLE 1, the variation of different metals in sediments from Dongzhai Harbor and several indices are listed. The analysis of the data depicted an order of metals accumulation in sediment that was Zn>

Pb>Cu> As>Cd. The data indicated that Zn was maximally accumulated in the sediments whereas Cd get least accumulation. The metal concentrations were compared to Primary Marine Sediment Quality criteria (GB 18668-2002) by State Environmental Protection Administration of China[7]. The average concentrations of the metals were far lower than the SQG values except for As. Most of them, including Zn, Pb, Cu and Cd, were close to background values while As surpass. The major contribution of anthropogenic metals in a marine coastal area is of terrestrial origin, i.e. from urban development and other human activities near the mangrove[8]. The low metal concentration in Dongzhai Harbor firstly due to the feature on absorb, deposit and settle down metals in mangrove ecosystems and also due to the less developed industry and a relatively low human population.

TABLE 1 : Major element concentrations and marine sediment quality guidelines, expressed as (mg/kg) dry weight

Sample ID	Cu	Zn	Pb	Cd	As	References
1#	4.80	50.52	13.90	0.001	18.43	
2#	2.50	22.61	8.09	0.001	17.80	
3#	2.21	24.91	15.42	0.002	16.84	This study
4#	6.12	47.14	9.43	0.04	16.50	
5#	2.38	21.09	6.13	0.002	14.46	
Guidelines for metals contamination in sediment						
UCC	25	71	34	0.098	1.6	Taylor,1995
ERL	34	150	46.7	1.2	8.2	Long et al,1995
ERM	270	410	218	9.6	70	
PMSQ	35	150	60	0.5	20	SEPA,2002

UCC: average concentrations of the upper continental crust

Effects range low (ERL) and effects range median (ERM) are SQGs developed to categorize the range of concentrations in sediment the effects of which are scarcely observed or predicted (below the ERL), occasionally observed (ERL-ERM), and frequently observed (above the ERM)[9]. Effects Range-Low (ERL) and Effects Range-Median (ERM) were the main parameters used to estimate the adverse biological effects of metals in the marine and estuary sediments and derived for the US National Oceanic and Atmospheric Administration (NOAA), with numerous types of modeling, laboratory and field studies performed on marine and estuarine sediments. Metal concentrations in sediments can be classified into three levels, namely rarely (<ERL), occasionally (ERL-ERM) and frequently (≥ERM) associated with adverse biological effects. Our results (TABLE 1) show that ERL was never exceeded but As in the study areas, and As concentrations were over ERL more than twice in almost five stations, which would likely not cause occasionally effects in the studied areas.

The pollution load index (*PLI*) was introduced to evaluate the level of metal contamination. The *PLI* is determined as the *n*th root of the *n* contamination factors (*Cf*$_n$) multiplied together and calculated using the following equation:

$$PLI = (Cf_1 \text{x } Cf_2 \text{x } Cf_3 \text{x } ..... CF_n)^{1/n} \tag{1}$$

The *Cf* for each metal is the ratio of the measured concentration in the sediment to the background value, which is classified into four grades for monitoring the pollution of one single metal over a certain period of time[10].

The *PLI* was applied to determine the integrated pollution status of the combined toxicant groups at the sampling stations. The *PLI* value >1 indicates a polluted condition, while *PLI*<1 signifies no metal pollution[11]. The spatial map of *PLI* in Figure 2 shows that the *PLI* results for all the stations ranged from 0.25to 0.72, and the highest *PLI* value of 0.72 occurred at station S4, suggesting that our studied region was no metal pollution.

The mean ERM quotient is calculated using the following formula:

$$\text{mean-ERM quotient} = \sum (C_x / ERM_x)/n \tag{2}$$

where C_x is the measured concentration of the examined component(*x*) in the sediment, ERM*x* is the ERM for metal *x*, and *n* is the number of metals. The mean- ERM quotients of less than or equal to 0.1 (low priority site) have a 9% probability of being toxic, quotients of 0.11-0.5 (medium-low priority site) have a 21% probability, quotients of 0.51-1.5 (high-medium priority site) have a 49% probability, and quotients of greater than 1.50 have a 76% probability. Based on the mERM-Q data (Figure 2), all the investigated stations had mERM-Q< 0.1(low priority site) varying within the range of 0.06-

0.09, and had a 9% probability of being toxic. Both the *PLI* and mERM-Q revealed that the highest potential ecological risk zone was found in northern and southern of bay.
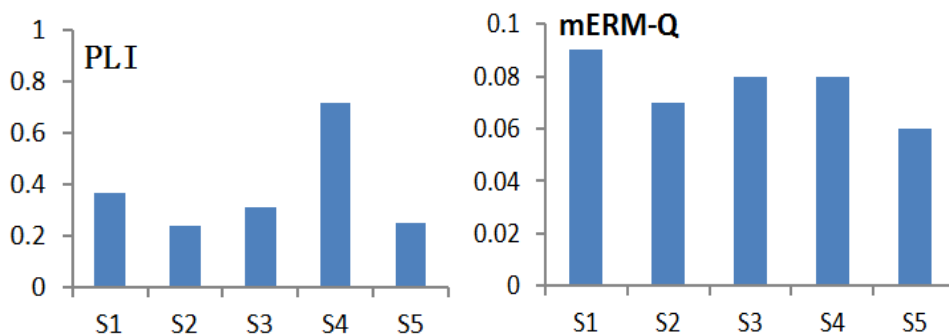

Figure 2 : The pollution load index (left) values and mERM-Q (right) values

The geoaccumulation factor for 5 elements was calculated according to the following equation, where BEn is geochemical background values of heavy metals and Cn is content of the element in sediments (a measured value, meaning mass ratio).

$$I_{geo} = \log_2{}^{[Cn/(1.5BEn)]} \tag{3}$$

The pollution classes, ranging from Class 0 ($I_{geo} \leq 0$, unpolluted), to Class 6 ($I_{geo} > 5$, extremely polluted) proposed were used for this evaluation. The results in TABLE 6 are showed index of geo-accumulation (I_{geo}) of Cu, Zn, Pb, Cd are low, however, that of As is 4, meaning a serious pollution. Overall, index of geo-accumulation of heavy metal in mangrove wetland is a slightly higher than that in bottom sediments of Dongzhai Harbor, consistent with the results of the single factor evaluation. For further potential pollution sources analysis, the PCA was applied.

TABLE 2 : Index of geo-accumulation （I_{geo}） and the pollution grades of heavy metals

	S1#		S2#		S3#		S4#		S5#		wetland#	
	I_{geo}	level	I_{geo}	level	I_{geo}	level	I_{geo}	level	I_{geo}	level	I_{geo}	level
Cu	-0.63	0	-1.57	0	-1.75	0	-0.28	0	-1.64	0	1.27	1
Zn	-0.06	0	-1.22	0	-1.08	0	-0.16	0	-1.32	0	0.12	1
Pb	-1.27	0	-2.05	0	-1.12	0	-1.83	0	-2.45	0	-0.81	0
Cd	-5.2	0	-5.1	0	-5.2	0	-1.0	0	-5.8	0	0.43	1
As	3.43	4	3.38	4	3.30	4	3.27	4	3.08	4	2.92	3

Pearson correlation and multivariate Principal Component Analysis (PCA) were performed on IBM SPSS 19.0 for Windows. The Pearson correlation analysis (CA) was used to evaluate the coefficients between all metals and biogenic elements. The logarithm-transformed data matrix was applied to the principal component analysis (PCA) to visualize potential pollution sources. Varimax rotation with Kalser normalization was chosen in PCA to maximize factor variance and to simplify the columns of the factor matrix. The Pearson correlation coefficient is significant for Pb-As, Zn-Cd, Zn-As($p<0.05$) and Cu-Zn, Cu-Cd($p<0.01$). These associations are obvious on the basis of pollution sources, indicating that these metals are closely related to each other and may have different anthropogenic or natural sources.

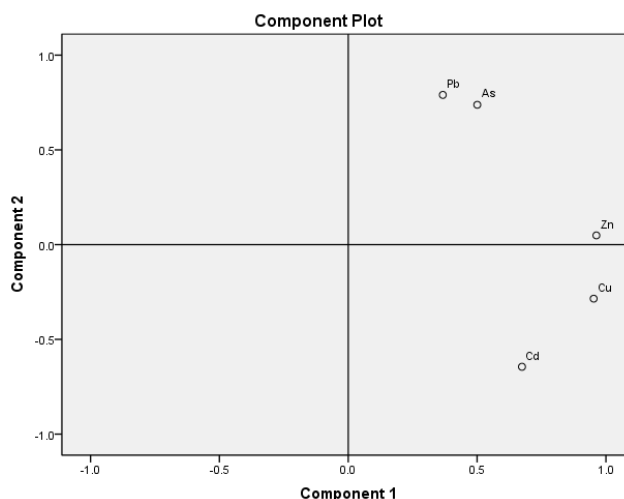**TABLE 3 : Pearson correlation coefficients**

	Cu	Pb	Zn	Cd	As
Cu	1				
Pb	0.091	1			
Zn	0.929**	0.362	1		
Cd	0.787**	-0.166	0.528*	1	
As	0.271	0.581*	0.476*	-0.136	1

Notes:* p < 0.05.and ** p < 0.01.

PCA was performed on the metal fractionation data, and the scores in the rotated principal component space are presented in TABLE 4. Two components were extracted which explain 85% of the total variance, and the eigenvalues >1. Almost selected metals were grouped together near the right side of the x-axis (Figure 3), which contributed high positive loadings to factor 1. The presence of Cu, Zn and Cd reflected the contribution of the natural geological sources of metals (e.g. weathered bedrock and corrosion product) into the coastal sediments. The sources of Pb and As infer that it mainly originates from effluents and wastes of human activities which affect the area such as aquaculture, and combustion of gasoline and diesel fuel by ships.

TABLE 4 : Results from principal component analysis based on metals

Factors	Variance explained by components	Percentages of total variance explained(%)
1	2.674	53.480
2	1.668	86.839
Rotated loading matrix		
Cu	0.952	-0.285
Pb	0.367	0.790
Zn	0.963	0.049
Cd	0.674	-0.645
As	0.501	0.738

Figure 3 : The principal component analysis loading plot of selected elements.

CONCLUSION

In the present study, different useful tools, methods, guidelines, and indices have been employed for the evaluation of the sediment pollution from the Dongzhai Harbor. The highest values of the contamination factor (marine sediment quality guidelines), pollution load index (*PLI*), geo-accumulation index (I_{geo}), and source factor (PCA) for all the selected metals were found in the study region. From the above results and discussion, it appears that As may occur occasional biological effect. Also, I_{geo} suggest there are serious pollution levels of As at all five stations. The pollution load index (PLI) and mERM-Q derived from the contamination factors shows that the potential ecological risk zone appear in northern and southern of Dongzhai Harbor. According to the factor analysis, the primary factor originates from natural sources. As and Pb resulted primarily from aquaculture, and combustion of gasoline and diesel fuel by ships. Numerous metals, including those elements considered highly toxic, such as Cu, Zn, Pb, Cd, As are stored in sediments of this mangrove ecosystem, which represents a potential ecotoxicological risk. According to guidelines previously established for the management and policy of sediment research, the development of public policy programs for restoration and recovery of natural resources, such as mangrove systems, must focus on the integration of socio-economic aspects and natural sciences.

ACKNOWLEDGEMENTS

REFERENCES

[1] X.Jiang, W.W.Wang, S.H.Wang, B.Zhang, J.C.Hu; Initial identification of heavy metals contamination in Taihu Lake, a eutrophic lake in China. Journal of Environmental Sciences **24**, 1539-1548 **(2012)**.

[2] G.Suresh, P.Sutharsan, V.Ramasamy, R.Venkatachalapathy; Assessment of spatial and potential ecological risk of the heavy metals in relation to granulometric contents of Veeranam lake sediments, India. Ecotoxicology and Environmental Safety **84**, 117-124 **(2012)**.

[3] D.Mackay; Multimedia environmental models: the fugacity approach, 2nd ed. CRC Press, USA 39-44 **(2001)**.

[4] S.Bayen; Occurrence, bioavailability and toxic effects of trace metals and organic contaminants in mangrove ecosystems: a review. Environ. Int. **48**, 84-101 **(2012)**.

[5] J.C.Fernández-Cadena, S.Andrade, C.L.Silva-Coello, R.De la Iglesia; Heavy metal concentration in mangrove surface sediments from the north-west coast of South America. Mar.Pollut.Bull. **82**, 221-226 **(2014)**.

[6] N.F.Tam, Y.S.Wong; Spatial variation of heavy metals in surface sediments of Hong Kong mangrove swamps. Environ. Pollut. **110**, 195–205 **(2000)**.

[7] SEPA (State Environmental Protection Administration of China), Marine Sediment Quality (GB 18668-2002); Standards Press of China, Beijing (in Chinese) **(2002)**.

[8] Qiu Yao-Wen, Yu Ke-Fu; Accumulation of heavy metals in sediment of mangrove wetland from Hainan Island. Journal of Tropical Oceanography, **30(2)**, 102-108 **(2011)**.

[9] E.R.Long, L.G.Morgan; The Potential for Biological Effects Of Sediment Sorbed Contaminants Tested in the National Status and Trends Program. NOAA Technical Memorandum NOS OMA 52. National Oceanic and Atmospheric Administration. Seattle, Washington **(1990)**.

[10] L.Hakanson; An ecological risk index for aquatic pollution control.asedimentological approach. Water Research **14,** 975-1001 **(1980)**.

[11] D.Tomlinson, J.Wilson, C.Harris, D.Jeffrey; Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. Helgol. Mar. Res. **33**, 566–575 **(1980)**.