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Spatial risk assessment and sources of heavy metals in surface sediments from Yangpu Port in the western Hainan Island

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ABSTRACT

Surface sediments collected from the largest port in Hainan Island, the Yangpu Port and its surrounding coastal area, were detected by inductively coupled plasma-mass spectrometry and atomic fluorescence spectrometry for Cu, Zn, Pb, Cd, and Hg, respectively. The present work attempts to determine the status of five heavy metals distribution in sediments, and their ecological risks' assessment in the studied area. Sediment quality guidelines (SQGs) and Hakanson's method were used to determine potential risk of heavy metal contamination. The results indicated that the mean contents of selected metals were never exceeded TEL, which would likely not cause occasionally effects in the studied areas. The calculated mean potential ecological risk degrees were in the descending order of Pb, Hg, Cd, Cu and Zn. Besides, multivariate statistical analyses revealed that Zn, Pb and Cu mainly originated from industrial waste water and sewage which were probably in the close relationship with characteristics about the Coastal industrial; Cd and Hg mainly derived from agricultural wastewater and oil leak. This research provides managers with information needed to better regulate the environment of the Yangpu Port.

KEYWORDS

Heavy metal; Risk assessment source analysis; Sediment; Yangpu port.

INTRODUCTION

As the most important places for human inhabitants, coastal zones are often polluted by various contaminants including heavy metals, which are a topic of concern because of their toxicity, persistence and biological accumulation in sediments[1,2]. The sediments function as a reservoir for metals act as natural and pollution sources of metals. The health status of marine sediments is an important criterion to evaluate the condition of aquatic environment, thus the determination metals in marine sediments is a significant procedure to understand the possible environmental changes caused by anthropogenic activities[3]. These metals once concentrations surpass certain thresholds in sediments may cause serious environmental problems due to their toxicity, wide source, non-biodegradable properties, and accumulation behaviors[4]. Therefore, 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.

With the rapid establishment of the Yangpu Economic Development Zone and the Yangpu Bonded Port, Yangpu Port as the national first class open port compels the further understanding of the distribution and potential risk of metals pollution in the west coast of Hainan Island, where the rapid economic and industrial development have been taken off and metal pollution has become a noticeable problem. To date, research regarding the metal distribution and risk assessment of sediments in this location remains scarce. In this paper, we report the first comprehensive study on spatial distributions, source identification and potential ecological risks of heavy metals in sediments from theYangpu Port. The outline of the present study were as follows (i) to reveal spatial distributions of heavy metals in surface sediments from the survey region,(ii) to study potential ecological risk of these heavy metals employing Hakanson's method with consideration of the model uncertainty, and (iii) to define the natural and/or anthropogenic sources of these heavy metals using combined multivariate statistical techniques.

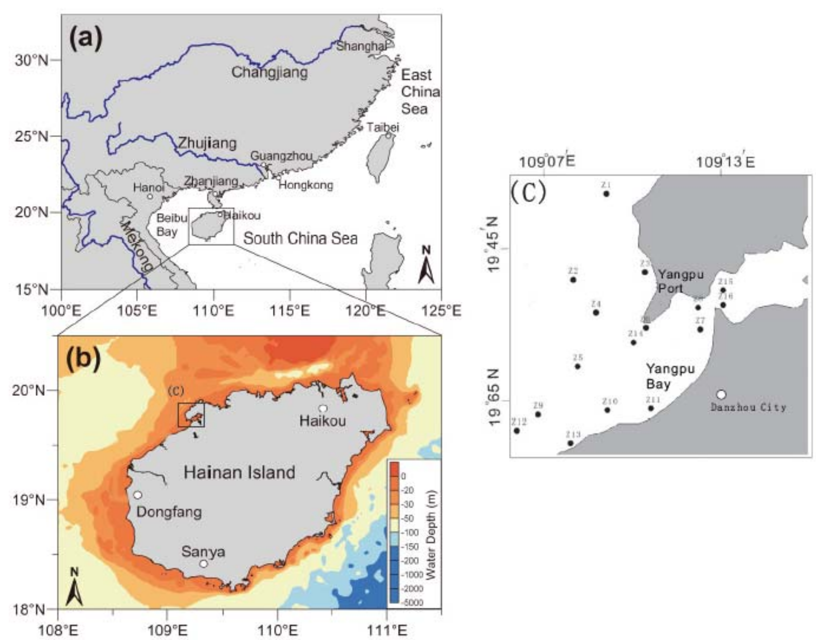

Figure 1 : Map of sampling stations in the Yangpu Port

MATERIALS AND METHODS

Analysis and quality control

Surface sediments were collected in triplicate using a Peterson grabs from 16 stations in Yangpu Port in November 2011 (Figure 1). The top 2 cm of sediments were removed with a polyethylene spatula, the three replicate samples well mixed, sealed in polyethylene bags. The collected sediments were kept at -20°C until further analysis. The dried sediments ground gently with an agate mortar and pestle, sieved through a 150 lm mesh for homogenization, and stored in sealed plastic bags. The concentrations of Cu, Zn, Pb, Cd, and Hg were all detected by means of inductively coupled plasma-mass spectrometry (ICP-MAS). Quality control was assured in the same way through the analysis of a marine sediment reference material (Offshore Marine Sediment, GBW 07314), duplicate samples and parallel samples. The analysis results were deemed reliable when repeat sample analysis error was below 5%, and the relative standard deviation of samples was within ±10%. The recovery rates for all of the metals between 90-120%. The results met the accuracy demand of the Chinese Technical Specification for Soil Environmental Monitoring HJ/T 166-2004.

Assessment method of sediment pollution

Sediment quality guidelines (SQGs)

Numerous sediment quality guidelines (SQGs) and different indexes have been developed to deal with environmental concerns. SQGs consist of the effects range low (ERL) and the effects range median (ERM) that are the main parameters for estimating the adverse biological effects of metals in marine and estuary sediments (Long et al.,1995). The ERL and ERM values, which depend on numerous toxicity tests, field studies, and altered benthic communities for sediment dwelling marine animals, are applied as guidelines for assessing the incidence of adverse biological effects of numerous pollutants, including metals, in marine sediments (Long et al.,1995).

All of the indexes applied above took into account the individual metals. Based on the fact that metals always occur in sediments as complex mixtures, the mean ERM quotient method was used to determine the possible biological effects of the combined toxicant groups, by computing the mean quotients for a large range of contaminants (Carr et al., 1996; Long, 2006). The mean ERM quotient is calculated using the following formula:

mean-ERM quotient=$\sum(C_x/ERM_x)/n$

where C_x is the measured concentration of the examined component (x) in the sediment, ERMx 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 (Long et al., 2000).

Potential ecological risk index (PERI)

To further screen sediment contamination degree caused by heavy metals, potential ecological risk index (PERI), which was developed based on sedimentary theory, was introduced to assess the ecological risk degree of metals in present sediments. Potential ecological risk index was originally proposed by Hakanson (1980) and widely used[6]. The value of E_{RI} can be calculated by the following formulas:

$$C_f^i = \frac{C^i}{C_n^i}, E_r^i = T_r^i \times C_f^i$$

$$E_{RI} = \sum_i^m E_r^i = \sum_i^m T_r^i \times \mathrm{C}_r^i = \sum_i^m T_r^i \times \frac{C_i}{\mathrm{C}_n^i}$$

where E_{RI} is the sum of the potential risk of individual heavy metal, E_{RI} is the potential risk of individual heavy metal, T_r^i is the toxic-response factor for a given heavy metal, C_f^i is the contamination factor, C^i is the present concentration of heavy metals in sediments, and C_n^i is the pre-industrial record of heavy metal concentration in sediments. Based on the Hakanson's approach, the toxic-response factors for Cu, Zn, Pb, Cd, Hg and Cr are 5, 1, 5, 30, 40 and 2 respectively. In this study area, the pre-industrial concentration records for Cu, Zn, Pb, Cd,Hg and Cr were replaced by their corresponding background values showed in TABLE 2. Hakanson defined five categories of E_r^i, and four categories of E_{RI}, as shown in TABLE 1.

TABLE 1 : Indices and corresponding degrees of potential ecological risk

E_r^i value	Grade of ecological Risk of single metal	E_{RI} value	Grades of potential ecological Risk of the environment
$E_r^i < 40$	Low risk	$E_{RI} < 150$	Low risk
$40 \le E_r^i < 80$	Moderate risk	$150 \le E_r^i < 300$	Moderate risk
$800 \le E_r^i < 160$	Consider risk	$300 \le E_r^i < 600$	Consider risk
$160 \le E_r^i < 320$	High risk	$E_{RI} \ge 600$	High risk

Multivariate analyses methods

Multivariate analyses of heavy metals contents in sediments were performed using Pearson's correlation analysis, Factor analysis (FA) by the software package SPSS version 19.0. The Pearson's correlation analysis is a method measuring the correlativity among heavy metals. FA is a kind of multivariate statistical analysis method and is utilized to reduce some complex variables to a few latent factors for analyzing relationships among the observed variables.

RESULTS AND DISCUSSION

Mean heavy metals concentration in surface sediments

The basic statistics for all heavy metal parameters measured during the sampling period at 16 typical sites as well as background values of the Yangpu Port[7], and corresponding values based on SQGs[5]were summarized in TABLE 2. According to the background values of metals in the Yangpu Port, it indicated that selected metal concentrations in surface sediments were all higher than their corresponding background values. Our results show that TEL was never exceeded but Pb in the study areas, which would likely not cause occasionally effects in the studied areas.

TABLE 2 : Summary statistics of heavy metal contents in surface sediments from the study region and guideline values of freshwater sediment quality mg/kg.

	Cu	Zn	Pb	Cd	Hg
Minimum	6.9	30.6	11.3	0.05	0.042
Maximum	28.3	116.9	35.5	0.20	0.006
Average	24.83	99.59	29.83	0.10	0.025
Background[a]	23.98	86.15	24.18	0.066	0.015
TEL[b]	35.7	123.1	35	0.596	0.174
PEL[c]	196.6	314.8	91.3	3.53	0.486

a Background: content in 1990s from Yangpu Port.(Yang and Zheng, 2008); b TEL: threshold effect level, dry weight (Smith et al., 1996); c PEL: probable effect level, dry weight (Smith et al., 1996).

Potential ecological risk assessment

Potential ecological risk assessment was applied to detect the potential ecological risk level of trace metals in sediments from the Yangpu Port. Calculated single element pollution factor, potential ecological risk of individual element and comprehensive potential ecological index were presented in TABLE 3, respectively. The calculated mean potential ecological risk degrees decreased in the order of Pb,Hg,Cd,Cu and Zn. That of 5 heavy metals was at low risk level. From the viewpoint of pollution level in every sampling site, the sampling sites at the highest risk degree caused by each heavy metal were Z6 for Zn,Z16 for Cd,Z5 for Pb,Z2 for Cu,Z10 for Hg respectively. Detailed comparisons were clearly presented in TABLE 4. The calculated E_{RI} values of every sampling site were in the descending order of Z15,Z7,Z2,Z14,Z13,Z4,Z3,Z10,Z11,Z8,Z9,Z5,Z12,Z16,Z6 and Z1.

Compared with the assessment results of SQGs, there was a similar assessment conclusion for Pb. However, these different conclusions on the contamination level of Hg proved that it was essential to synthesize different assessing methods to reduce the uncertainty among these assessing models and to supply more comprehensive information for policy-makers.

From overall regional analysis, the potential ecological hazards in Yangpu Port are higher in inshore than far shore, indicating that the construction and development of Yangpu Port has its impact on the distribution of heavy metals. Compared to other domestic typical Minato potential ecological risks results, the metals in Yangpu port such as Zn, Pb have relative high degree of ecological harm, but the overall potential ecological risk is fewer hazards.

TABLE 3 : Basic statistic of potential ecological risk assessment (PERI) of heavy metals in surface sediments from the study region.

Sample sites	E_r^i					E_{RI}
	Zn	**Cd**	**Pb**	**Cu**	**Hg**	
Z1	0.38	1.60	3.14	0.65	1.20	6.97
Z2	1.07	2.60	4.16	4.72	6.20	18.74
Z3	1.28	4.00	4.48	2.42	4.60	16.77
Z4	1.31	1.40	5.60	2.22	7.20	17.72
Z5	1.25	1.60	7.02	2.30	2.00	14.17
Z6	1.46	2.60	2.26	2.07	1.40	9.79
Z7	1.33	1.60	5.48	1.97	8.40	18.78
Z8	1.25	1.80	5.08	2.40	4.20	14.73
Z9	1.01	1.00	4.82	1.45	6.40	14.68
Z10	0.85	1.00	4.06	1.28	8.20	15.40
Z11	1.23	2.40	5.72	2.28	3.60	15.23
Z12	1.17	1.60	3.76	2.40	5.00	13.93
Z13	0.62	1.60	6.64	2.05	7.00	17.91
Z14	1.01	7.60	5.16	1.48	3.40	18.65
Z15	0.92	7.60	6.58	1.40	2.80	19.30
Z16	0.16	4.40	1.60	0.07	4.40	10.63
Average	1.02	2.78	4.72	1.95	4.75	15.21
Bohai bay[8]	1.09	60.44	7.16	5.10	17.80	99.79

Daya bay[9]	0.47	0.87	1.64	2.50	16.00	27.88

Sources identification based on multivariate statistical analyses

Statistical analysis was carried out with the purpose of exploring possible associations among total content of metals in sediments (TABLE 4). The Pearson correlation coefficient is significant for Pb-Zn, Cu-Zn and Cu-Pb ($p<0.01$); Hg-Zn, Pb-Hg ($p<0.05$). These associations are expected on the basis of pollution sources, indicating that these metals are associated with each other and may have different natural or anthropogenic sources.

TABLE 4: Pearson correlation coefficients between heavy metals

	Zn	Cd	Pb	Cu	Hg
Zn	1				
Cd	0.401	1			
Pb	0.680**	0.426	1		
Cu	0.929**	0.430	0.890**	1	
Hg	0.587*	0.320	0.528*	0.329	1

***Coefficients at 0.05 significance level, p < 0.05; ** Coefficients at 0.01 significance level, p < 0.01.**

The KMO test value (0.631) showed that the heavy metal concentration data in sediments from the study region are suitable for factor analysis (FA). FA was applied to the data sets (5 variables) separately for the 16 typical sampling sites to identify sources of heavy metals in sediments from theYangpu port by employing varimax rotation with Kaiser Normalization. By extracting the eigenvalues (>1) and eigenvectors from the correlation matrix, the number of significant factors and the percent of variance explained by each of them were calculated. Total variance of heavy metals contents and rotation component matrix for heavy metal contents were showed in TABLE 5.

TABLE 5 : Results from principal component analysis based on metals

Factors	Component	
	PC1	PC2
Rotated loading matrix		
Cu	0.749	-0.285
Pb	0.674	0.790
Zn	0.963	0.049
Cd	0.467	-0.645
Hg	0.401	0.738
Eigenvalue	2.442	1.614
% of variance explained	43.831	26.2760
% of cumulative	43.831	70.107

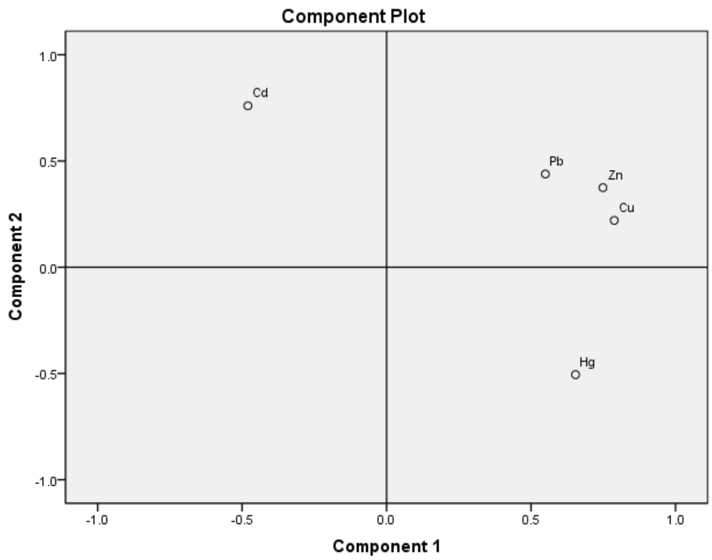

Figure 2 : The principal component analysis loading plot of metallic elements.

Principal component analysis extracted two common factors that describe more than 70% of the total data variability. Most of the elements were grouped together near the right side of the x-axis (Figure 2), which contributed high positive loadings to factor 1. First component (PC1) explained 43.831% of the total variance loaded heavily on Zn, Pb and Cu. Factor 2, dominated by Hg and Cd, accounted for 26.2760% of the total variance. The results of FA were well matched with the results of Pearson correlation analysis. The presence of Cu, Zn and Pb can be attributed to effluents and wastes of human activities such as industrial wastewater, sewage. Most of the pesticide chemical composition contains the heavy metals such as Cd and Hg, so PC2 main from agricultural residues and post-fertilization.

CONCLUSIONS

In this work, 5 heavy metals in surface sediments from the Yangpu port were investigated. Then spatial risk assessment at the screening level and source apportionment of these heavy metals were studied based on geostatistics methods, SQGs, Hakanson's method and integrated multivariate statistical methods (Pearson's correlation analysis and FA included). The mean concentrations of studied heavy metals all exceeded the geochemical background values of the Yangpu port. According to the results based on SQGs and Hakanson's method, Pb were identified as the priority metal pollutants of concern. Multivariate statistical analyses showed Zn, Pb and Cu mainly originated from wastewater and industrial wastewater. Cd and Hg mainly derived from agricultural wastewater and oil leak. The spatial characteristics of heavy metals content are higher in inshore than far shore, indicating that the construction and development of Yangpu Port has its impact on the distribution of heavy metals. Therefore, the measures, to develop strategies of contamination control and management with the comprehensive consideration of the entire basin and to optimize industrial structure of the corresponding cities, are required for human health protection and future restoration of the water of Yangpu port.

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