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The spatial multiscale variability of heavy metals based on factorial kriging analysis: A case study in the northeastern Beibu Gulf

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Abstract

Factorial kriging analysis is applied to the research on the spatial multiscale variability of heavy metals in submarine. It is used to analyze the multiscale spatial structures of seven heavy metals, Ni, Cu, Zn, Pb, Cr, As and Cd in the surface sediment from the northeastern of Beibu Gulf, identify and separate spatial variations at different scales of heavy metals, and discuss the provenance of heavy metals and the influencing factors. The results show that the existence of three-scale spatial variations those consist of nugget effect, a spherical structure with range of 30 km (short-range scale) and a spherical structure with range of 140 km (long-range scale) in the linear model of coregionalization fitted. The spatial distribution features of seven heavy metals at short-range scale reflect "spot-like" or "stripe-like" local-scale spatial variations; the spatial distribution features of the seven heavy metals at long-range scale represent "slice-like" regional-scale spatial variations. At local scale, Zn, Cr, Ni, Cu, Pb and Cd are derived primarily from parent materials of Hainan Island, Leizhou Peninsula and Guangxi land, whose spatial distribution characteristics are controlled by granularity of sediments, while As is influenced dominantly by human pollution components from Hainan Island and Leizhou Peninsula. At regional scale, Zn, Cr, Ni and Cu originate primarily from parent rock materials of Leizhou Peninsula and Hainan Island, secondly from Guangxi land; As originated primarily from parent rock materials from Hainan Island, secondly from Leizhou Peninsula and Guangxi land. These metals are transported and migrated with sediments dominated by the anticlockwise circulation of Beibu Gulf year-round, deposited in "convergence center", forming the whole sedimentary pattern in direction of NWW-NNW at regional scale. The difference in distribution type between As and other metals at regional scale is mainly due to their different geochemical behavior.

Key words: spatial multiscale variability, heavy metals, factorial kriging analysis, sediments, northeastern Beibu Gulf

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1 Introduction

Heavy metals in marine sediments have drawn widely attention because of their ecological and environmental importance (Yu et al., 2008; Pan and Wang, 2012; Wang et al., 2013). Heavy metals in sediments are derived from different natural and anthropogenic sources (Irabien and Velasco, 1999; Xia et al., 2011; Varol and Sen, 2012; Dou et al., 2013; Gu et al., 2012; Gan et al., 2013). Moreover, the sedimentary process after sediments entering the sea is affected by topography, current, redox conditions and so on. Different sources and influence factors, acted at different spatial scales, dominate different scales spatial variations of heavy metals, indicating multiscale spatial variations characteristics. It also could reveal the different sources of heavy metals and the influence factors by identifying their spatial variations at different scales. In general, the spatial variations at short-range scale of heavy metals indicate the influence of human activities, while the spatial variations at the long-range scale are dominated by the parent rock materials of source areas (Sollitto et al., 2010; Lv et al., 2013).

For a long time, multiscale spatial variations of heavy metals in submarine have not drawn enough attention. Previous studies were mostly based on traditional statistical methods and focused

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on some indexes, such as sediment quality guidelines, enrichment factor, geological accumulation indicators (Lin et al., 2011; Xia et al., 2011; Gu et al., 2012; Dou et al., 2013; Hu et al., 2013), to study the enrichment level and estimate the sources of heavy metals. Factully, these indexes represent relative amount of heavy metals, superimposed by complex information with multi-sources and multiscales, which are difficult to reveal the truth of spatial distribution and the enrichment level. Therefore, it is necessary to study the spatial variations of heavy metals at different scales.

It has been proved that geostatistics is an effective tool for research on the spatial variation and pattern (Goovaerts, 1997). Compared with traditional statistical methods, geostatistics accounts for the spatial location information of the data and can effectively reveal the spatial structure information of the geochemical data. There are many geostatistic methods, such as simple kriging, ordinary kriging, cokriging and so on. Factorial kriging analysis (FKA), combined with multivariate principal component analysis and geostatistics, could describe and separate the spatial variation characteristics of different scales and summarize the main feature of each spatial scale by fitting the linear model of coregionalization (LMC) and cokriging interpolation (Goovaerts, 1992). Recently, FKA has been applied widely to model the multiscale spatial variations of heavy metals, nutrients, geophysical and geochemical properties in soils (Goovaerts and Webster, 1994; Castrignanò et al., 2000; Sollitto et al., 2010; Lv et al., 2013), and has become a powerful tool for soil and environmental research.

This paper reports the geochemical data of seven heavy metals, Ni, Cu, Zn, Pb, Cr, As and Cd from surface sediments in the northeastern Beibu Gulf. On the basis of the factorial kriging analysis, the aim of the study is: (1) to investigate the spatial structures of heavy metals; (2) to interpret spatial variations at different scales; and (3) to discuss the provenance of heavy metals and the dominating factors at each scale.

2 Materials and methods

2.1 *Study area*

The Beibu Gulf, located in the northwest of the South China Sea, is characterized by tropical-subtropical monsoon climate

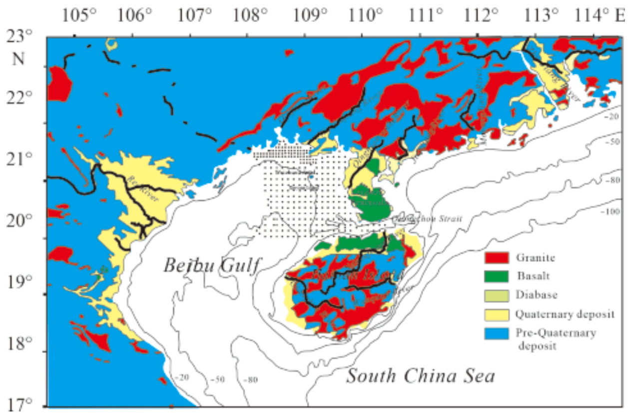

Fig. 1. Lithology distribution in adjacent regions of the Beibu Gulf and sampling stations (black spots) (modified from Xu (2014)).

with average temperature of 23°C and annual precipitation of 1 300–2 500 ml①. The Beibu Gulf is surrounded by land in the west, north and east coast, with the deepest water of 100 m. A large number of rivers flow into Beibu Gulf, such as the Red River, the Qinjiang River, the Nanliu River, the Qingnianyun River, the Nandu River, the Changhua River and so on (Fig.1), which are the main material suppliers to the study area by carrying huge amount of sediments into the gulf. Surface current of the Beibu Gulf performed as a large anticlockwise circulation both in winter and summer (Fig. 2) (Sun, 2005; Chen et al., 2011) and the flow direction does not change with monsoon.

Geologically (Fig. 1), to the north coast of the study area, Pre-Quaternary sedimentary rock is distributed widely in Guangxi land, with granites in NE-SW direction, and Quaternary loose sediments are distributed around Beihai City. To the east coast, the Leizhou Peninsula, is divided into two sections where the north is distributed with Quaternary loose sediments, while the south is a large area of Late Quaternary basalts. To the south coast, Hainan Island, Late Quaternary basalts are distributed widely in the north, and granites and Pre-Quaternary sedimentary rocks are exposed in the middle of the island, with Quatern-

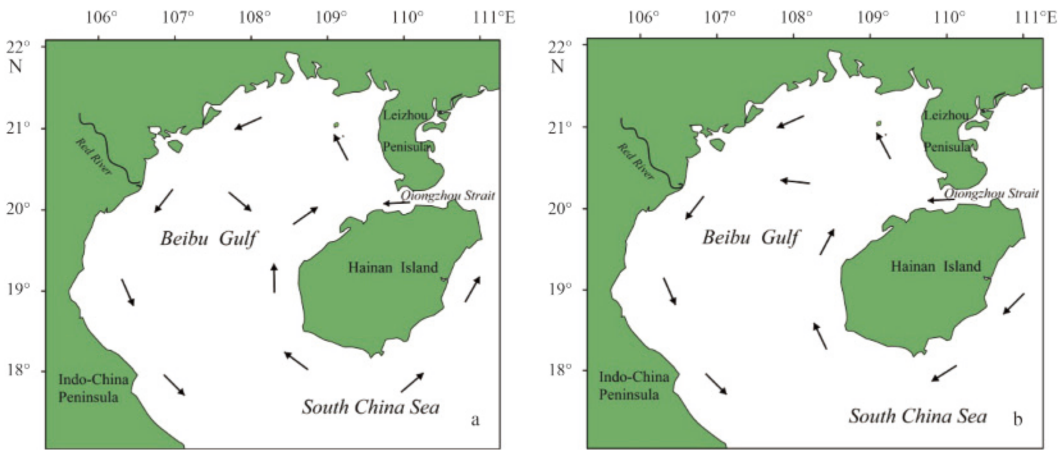

Fig. 2. Sketch map of surface current in summer (a) and winter (b) of the Beibu Gulf (modified from Sun (2005) and Chen et al. (2011)).

① The Second Institute of Oceanography, SOA, 2010. Surveys and research report of seabed sediment in CJ16 area (in Chinese).

ary deposits in the coastal area. To the west coast, there is plenty of the Pre-Quaternary sedimentary rock distributed, with some intrusive rocks exposed along the Red River Fault and Quaternary loose sediments in the Red River Delta.

2.2 *Samples and chemical analysis*

A total of 307 surface samples (0–5 cm) were collected from the northeastern Beibu Gulf using grab samplers during "908" survey in June and July 2007 (Fig. 1). After sampling, all samples were stored at 4°C. Prior to chemical analysis, the samples were dried below 105°C, grinding to 200 meshes by agate, and stored in clean plastic bags at room temperature.

For acid digestion, 0.25 g of powered sample was put in a teflon bomb with an acid mixture (5:4:1 $V(HNO_3)$ + $V(HCl)$ + $V(HF)$) (Loring and Rantala, 1992) and then heated to 120°C for 12 h on a heating plate. The acid digestion was repeated until only a negligible amount of white residue remained. Afterwards, the solution was evaporated to dry and extracted with HNO_3. For element analysis, Cr, Cu, Zn, Ni, Cd and Pb concentrations were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). As concentration was analyzed by Atomic Fluorescence Spectrometry (AFS). Blanks and China standard reference materials (GSS1, GSS2, GSD9, GSD10, GBW07313) were included in the analyses for data quality control. The results show that the relative standard deviation is with a variation of <10% approximately (mostly <5%).

2.3 *Factorial kriging analysis*

FKA has been introduced in details by many previous studies (Wackernagel, 1994; Goovaerts and Webster, 1994; Goovaerts, 1992, 1997; Castrignanò et al., 2000). It is used to analyze the interrelationships between variables at different spatial scales through fitting the linear model of coregionalization (LMC), and to estimate the principal components at each given scale.

In the linear model of coregionalization, the direct- and cross-variograms of all the *n* variables, are modeled as the sums of variograms at each scale, and can be defined as the linear combination of basic functions. The LMC can be written as the matrix term:

$$\gamma(h) = |\gamma_{ij}(h)| = \sum_{u=1}^{Ns} B^u g^u(h). \tag{1}$$

MatLab program is used to analyze the direct- and cross-variograms, $\gamma_{ij}(h)$, of heavy metals, from which spatial structure parameters are obtained. $B^u = [b^u{}_{ij}]$, called coregionalization matrix, which is a symmetric positive semi-definite matrix of order $n \times n$, describes the relationships between *n* variables at given scale $\mu \cdot g^u(h)$ is the basic variogram function, which could be chosen according to the spatial structures, such as spherical model, exponential model, linear model and so on (Oliver, 1987).

The iterative algorithm proposed by Xavier (2010is used to fit the LMC, from which B^u can be obtained. Principal component analysis (PCA) was carried on each coregionalization matrix, which generated a set of principal components, called coregionalization factors, and the spatial patterns of different scales can thus be separated (Webster, 1985).

On basis of the multiscales spatial structures of heavy metals, kriging interpolation was conducted to obtain the spatial distribution characteristics at each scale.

3 Results

3.1 *Statistical characteristics of heavy metals in the northeastern Beibu Gulf*

The statistical results (Table 1) show that the concentration ranges of seven heavy metals, Ni, Cu, Zn, Pb, Cr, As and Cd, are 1.00–61.70, 2.00–59.00, 7.00–116.00, 6.00–112.60, 6.00–106.00, 1.60–97.50 and 0.02–0.28 mg/kg, respectively, with average concentrations of 24.97, 17.10, 70.60, 28.38, 63.14, 11.38 and 0.08 mg/kg, respectively. The average concentrations of seven heavy metals are below the primary marine sediment quality standard (CSBTS, 2002), indicating an overall good water quality in the study area. However, concentrations of As in many stations have exceeded the secondary marine sediment quality standard (65.00 mg/kg) (CSBTS, 2002), suggesting an influence of anthropogenic pollution.

From the pearson correlation matrix (Table 2), it can be seen that except As, a significant correlation (r>0.6, P=0.01) exists among Ni, Cu, Zn, Pb, Cr and Cd. At the same time, significant correlation (r>0.5, P=0.01) exists between the heavy metals, Ni, Cu, Zn, Pb, Cr and Cd, and constant elements Al_2O_3, Fe_2O_3, and organic carbon, indicating a close relationship among clay particulate materials, organic matter and heavy metals of Ni, Cu, Zn, Pb, Cr and Cd. There is significant correlation between As and MnO (r=0.58, P=0.01), and no correlation between As and Al_2O_3 (r=–0.12, P=0.05) as well as MnO and Al_2O_3 (r=0.02).

3.2 *Spatial structural characteristics of heavy metals and linear model of coregionlization*

Based on MatLab program, the direct- and cross-variograms analyses were carried on seven heavy metals (Fig. 3). The results show the variograms of Zn, Cr, Ni, Cu, Pb, As and Cd display three structures: nugget effect, a spherical structure with range of 30 km (short-range scale) and a spherical structure with range of 140 km (long-range scale).

There is a positive intercept in every variogram curve, named nugget variance, which represents the influence of sampling error and measurement error as well as random variation (Oliver, 1987). At short-range scale (30 km), direct- and cross variograms values of each metal increase rapidly with distance, which reflects a larger variation and the inhomogeneity of the metal concentration. At long-range scale (140 km), direct- and cross-vari-

Table 1. Statistical results of seven heavy metals in surface sediments of study area

Location		c(Cr)/ mg·kg^{-1}	c(Cu)/ mg·kg^{-1}	c(Zn)/ mg·kg^{-1}	c(Ni)/ mg·kg^{-1}	c(Cd)/ mg·kg^{-1}	c(Pb)/ mg·kg^{-1}	c(As)/ mg·kg^{-1}	Reference
Northeastern Beibu Gulf	range average	6.00–106.00(63.14)	2.00–59.00(17.10)	7.00–116.00(70.06)	1.00–61.70(24.97)	0.02–0.28(0.08)	6.00–112.60(28.38)	1.60–97.50(11.38)	this study
Primary standard, China	average	80.00	35.00	150.00	nd	0.50	60.00	20.00	CSBTS (2002)
Second standard, China	average	150.00	100.00	350.00	nd	1.50	130.00	65.00	CSBTS (2002)

Notes: The c represents the concentration; and nd means not determined.

Table 2. Pearson correlation matrix of heavy metals with constant elements of study area

	$c(Al_2O_3)$	$c(Fe_2O_3)$	c(MnO)	c(org C)	c(Ni)	c(Pb)	c(Cu)	c(Zn)	c(Cr)	c(As)	c(Cd)
$c(Al_2O_3)$	1.00										
$c(Fe_2O_3)$	0.61[1)]	1.00									
c(MnO)	0.02	0.51[1)]	1.00								
c(org C)	0.90[1)]	0.49[1)]	-0.01	1.00							
c(Ni)	0.82[1)]	0.79[1)]	0.35[1)]	0.76[1)]	1.00						
c(Pb)	0.63[1)]	0.82[1)]	0.44[1)]	0.55[1)]	0.71[1)]	1.00					
c(Cu)	0.74[1)]	0.64[1)]	0.19[1)]	0.68[1)]	0.84[1)]	0.70[1)]	1.00				
c(Zn)	0.74[1)]	0.67[1)]	0.22[1)]	0.72[1)]	0.89[1)]	0.69[1)]	0.83[1)]	1.00			
c(Cr)	0.80[1)]	0.83[1)]	0.31[1)]	0.68[1)]	0.94[1)]	0.76[1)]	0.85[1)]	0.84[1)]	1.00		
c(As)	-0.12[2)]	0.40[1)]	0.58[1)]	-0.14[2)]	0.07	0.43[1)]	0.05	0.03	0.09	1.00	
c(Cd)	0.68[1)]	0.65[1)]	0.35[1)]	0.67[1)]	0.76[1)]	0.78[1)]	0.75[1)]	0.77[1)]	0.75[1)]	0.20	1.00

Notes: The c (org C) represents the organic carbon concentration; [1)] indicates that the correlation is significant at the 0.01 level (2-tailed); and [2)] indicates that the correlation is significant at the 0.05 level (2-tailed).

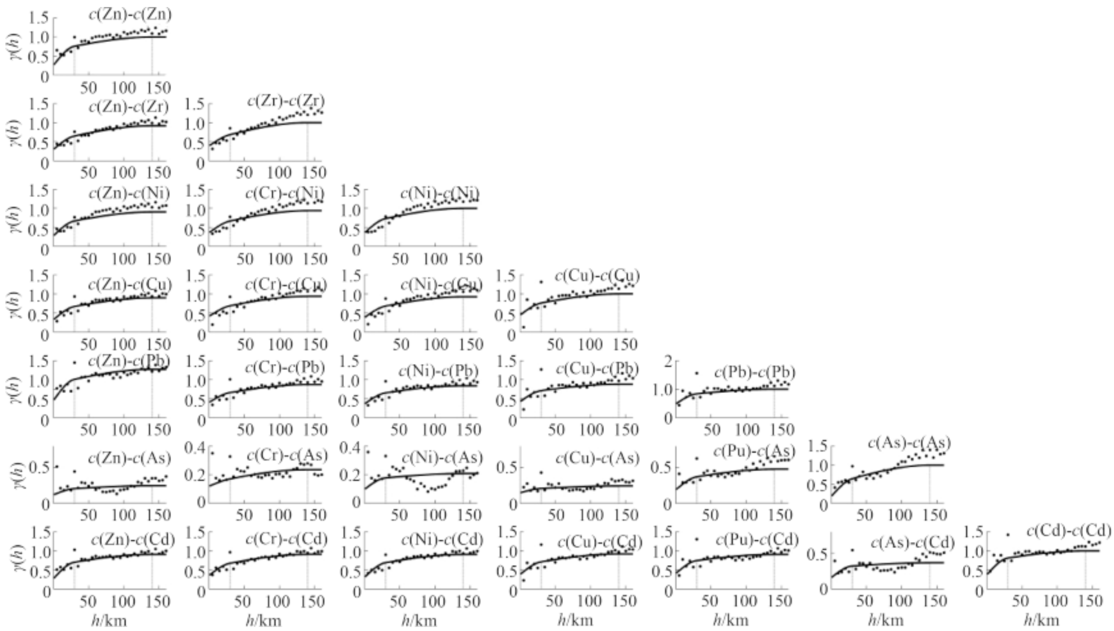

Fig. 3. Direct- and cross-variograms matrix plot of seven heavy metals in study area (the black spots represent experimental variogram values; solid line represents the variogram curve fitted).

ograms values of each metal increase gradually, which illustrates a weaker variation of metal concentration and a more uniform distribution.

Based on variogram analysis, the linear model of coregionalization (LCM) can be written as follows:

$$\begin{cases} \gamma_{ij}(h)=C_0, h=0, \\ \gamma_{ij}(h)=C_0+b^1{}_{ij}\left[\frac{3}{2}\left(\frac{h}{30}\right)-\frac{1}{2}\left(\frac{h}{30}\right)^3\right]+ \\ \qquad b^2{}_{ij}\left[\frac{3}{2}\left(\frac{h}{140}\right)-\frac{1}{2}\left(\frac{h}{140}\right)^3\right], \\ \qquad 0<h\leqslant 140\ km, \\ \gamma_{ij}(h)=C_0+b^1{}_{ij}+b^2{}_{ij}, h>140\ \text{km}, \end{cases} \quad (2)$$

where C_0 is the nugget variances. $B^u=[b^u{}_{ij}]$ is obtained by use of the multi-Gaussian Iterative algorithm proposed by Emery (2010).

3.3 *Spatial principal components of heavy metals at different scales*

The PCA of coregionalization matrix of nugget shows the variance contribution of the two primary principal components reaches 94.08% of the total variance (Fig. 4a). However, there is no higher loading between heavy metals and factors F_1, F_2. Nugget variance represents not only variation at microscale, but also contains sampling errors and test errors. As a result, there is no significant correlation between the heavy metals and the two primary principal components, and discussion would be focused on variations at short-range and long-range scales

The PCA of coregionalization matrix at short-range scale shows that (Fig. 4b) the variance contribution of the two primary principal components reaches 97.29% of the total variance. Factor F_1 explains 81.33% of the total variance, where higher loadings (>0.5) exist between Zn, Cr, Ni, Cu, Pb, Cd concentrations and F_1. Factor F_2 explains 15.96% of the total variance, with a higher loading of As concentration on F_2. Meanwhile, Pb concentration shows a moderate negative loading (–0.31) on F_2,

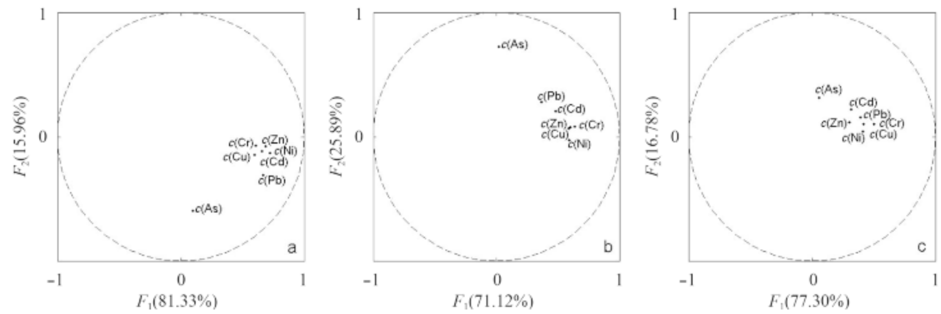

Fig. 4. Plots of principal component correlations at nugget scale (a), short-range scale (b) and long-range scale (c).

which suggests a double effect of F_1 and F_2 on Pb concentration.

It can be seen from the PCA of coregionalization matrix at long-range scale that (Fig. 4c), the variance contribution of the two primary principal components accounted for 97.01% of the total variance. Factor F_1 explained 71.12% of the total variance, where higher loadings (>0.5) exist between Zn, Cr, Ni, Cu concentrations and F_1, with moderate loadings of Pb concentration (0.37) and Cd concentration (0.48). Factor F_2 explains 25.89% of the total variance, in which As concentration shows a higher loading (0.72).

3.4 *Spatial multiscale distribution characteristics of heavy metals*

At short-range scale (30 km), the spatial distribution patterns of Zn, Cr, Ni, Cu, Pb and Cd concentrations are similar to each other (Fig. 5), in which high-value areas display as “spot” or “stripe”, with concentrations changing largely and heterogeneously, reflecting the spatial variations at local scale. The high-value areas distribute mainly in Wushi Harbor, west of Leizhou Pennisula, Beihai Bay, the south sea of Fangchenggang, Haikou Port and the area around Weizhou Island. Meanwhile, another high-value banded area extends in NS-direction from the northwestern sea of Hainan Island towards Weizhou Island and Xieyang Island. The low-value areas distribute mainly in the north of the study area from Anpu Port to Qinzhou Port (except the Beihai Bay), the Qiongzhou Strait and the southwest area of the study area. The high-value areas of As concentration distribute mostly in the Chengmai Bay, the Haikou Bay, the west mouth of the Qiongzhou Strait, Jianghong Town and nearby, Xieyang Island, secondly in the northern area from Beihai City to Fangchenggang along Guangxi coast. Concentrations of As in these areas (>20 mg/kg) have exceeded the primary marine sediments quality standard (Table 1), and As concentrations at many locations have exceeded the secondary marine sediments quality standard, which suggest the influence of anthropogenic pollution.

At long-range scale (140 km), all the metals show the “slice-like” high-value areas, with concentrations changing gently and the evident directional distribution, representing the regional-scale spatial variations (Fig. 6). The high-value areas of Zn ,Cr, Ni, Cu and Cd concentrations stretched from Wushi Port towards the west, distributed in a overall WNW direction, and intersected in south of Weizhou Island with a extending northward higher value area from the northwest of Hainan Island. It can be concluded that these heavy metals (Zn, Cr, Ni, Cu and Cd) originated primarily from the Leizhou Pennisula and Hainan Island, secondly from Guangxi land. As concentration distribution is different from other metals, whose high-value areas extend in the NNW direction from the north of Hainan Island towards the Leizhou Peninsula, and the highest value is located in the area from Haikou Port extending the northwest to west export of the Qiongzhou Strait. It can speculate that Hainan Island is the main provenance area of As. Besides, it is inferred that another high-value area of As concentration, in coastal zone of Beihai City to Fangchenggang along Guangxi, is influenced by Guangxi land. The distribution of Pb concentration, in NW direction, is in the between of the above two. The high-value area of Pb concentration extends from the northwest of Hainan Island in NE direction to Wushi Port and turns to NW direction of the Leizhou Peninsula, suggested that Pb comes primarily from Hainan Island, the Leizhou Peninsula, secondly from Guangxi land.

4 Discussion

4.1 *Provenance of heavy metals and its influencing factors at local scale*

The spatial variations of heavy metals at local scale remove the influences of the spatial variations at other scales (regional and background), which indicates the distinctive natural and anthropogenic influence.

At local scale, Zn, Cr, Ni, Cu, Pb and Cd are derived mainly from parent rock materials. Spatially, the high-value areas correspond to the areas of larger mean size (Φ>5, d<0.032 mm) and lower sand percentage (<20%). Meanwhile, the low-value areas are in good agreement with the areas with smaller mean size (Φ<4, d>0.063 mm) and higher sand percentage (>40%) (Tong et al., 2012)(Fig. 7). It demonstrates the influence of sediment granularity on heavy metal distribution. Compared with coarse sand sediments, clay particulate materials have smaller particle size, larger surface area and stronger adsorption, and are primary carriers of heavy metals into the ocean (Ip et al., 2007; Yu et al., 2008). The higher correlation between the heavy metals concentrations (Cu, Ni, Zn, Cr, Cd, and part of Pb) and clay materials concentrations (Table 2) illustrates the source of rock composition.

The distribution of As concentration is controlled by anthropogenic pollutants. As could be created largely from human activities, such as the usage of insecticides, herbicides, phosphorus fertilizer in the agriculture production, paints and pigments, leaded gasoline production, burning of fossil fuels, mining and smelting of arsenic ore in industry (Flynn et al., 2002; Smedley and Kinniburgh, 2002; Paul et al., 2009). The high-value areas of As concentration, the Chengmai Bay, the Haikou Bay, Jianghong Town, the Beihai Bay and Fangchenggang, are the areas suffered from heavy population and strong human activities, with serious industrial and municipal sewage (Zhang and Lan, 2012; Gu et al., 2012). Recently, mining activities of Shilu iron-rich multimetal

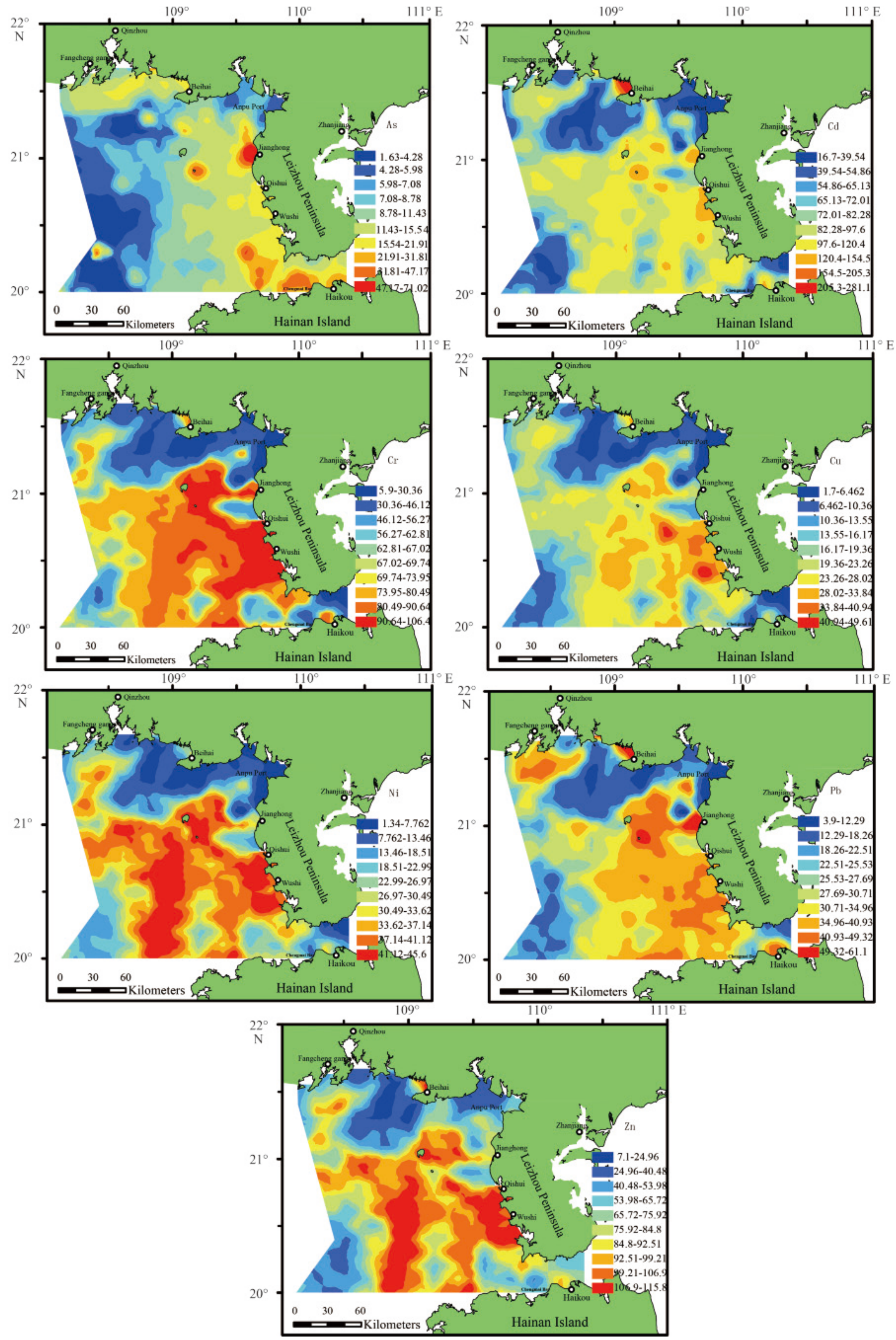

Fig. 5. Spatial distribution plots of sevev heavy metals at local scale (Zn, Cr, Ni, Cu, Pb and As concentrations in unit of mg/kg; Cd concentration in unit of μg/kg).

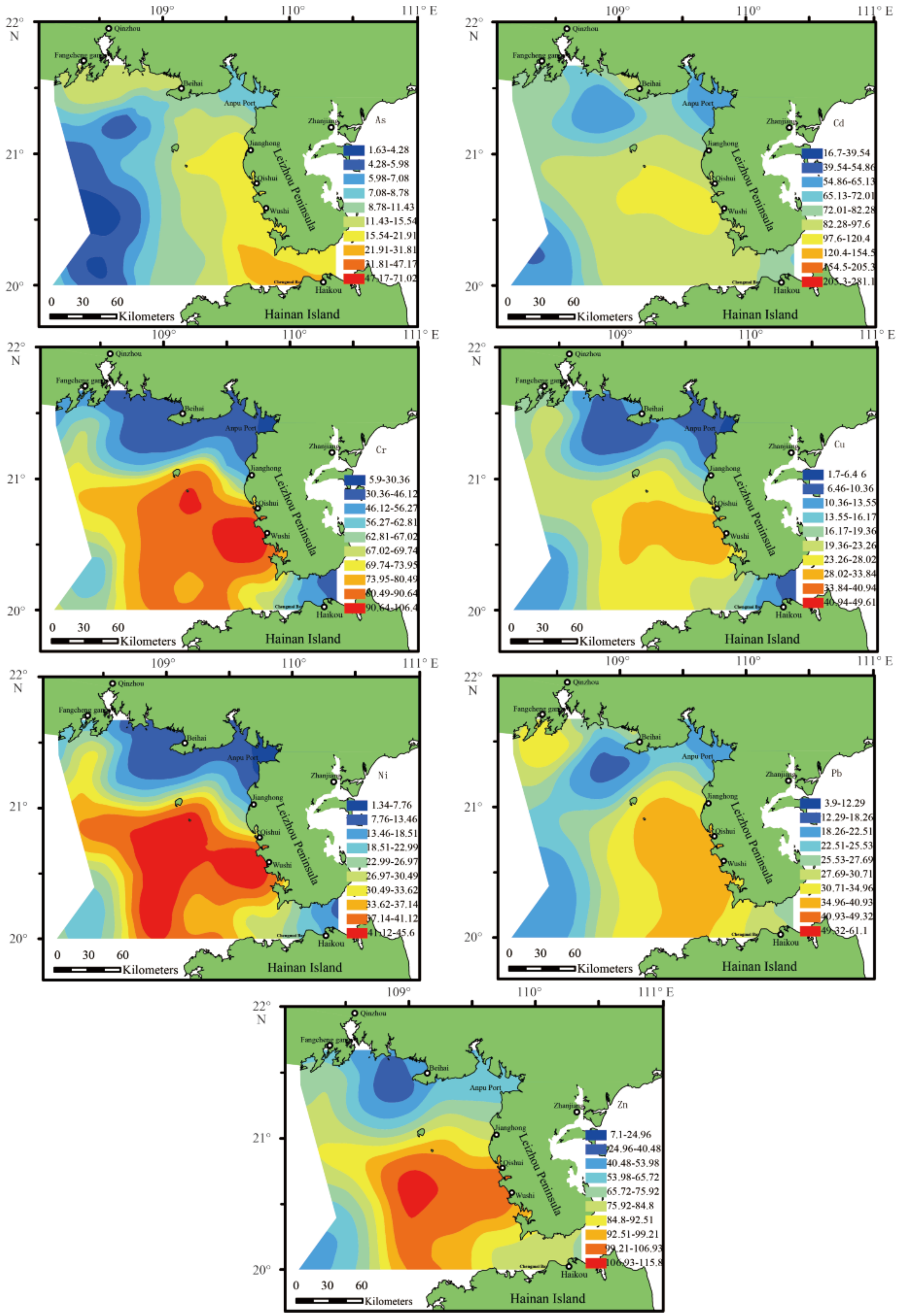

Fig. 6. Spatial distribution plots of seven heavy metals at regional scale (Zn, Cr, Ni, Cu, Pb and As concentrations in unit of mg/kg; Cd concentration in unit of μg/kg).

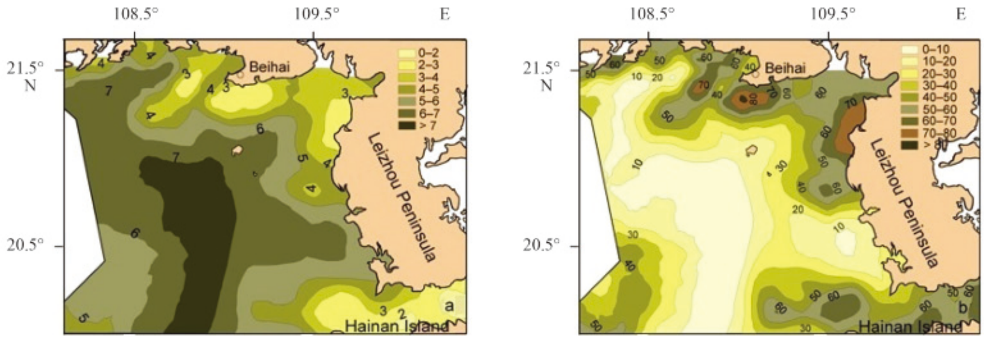

Fig. 7. Mean size (Φ) (a) and sand percentage (%) (b) in surface sediments of Beibu Gulf (modified from Tong et al., 2012).

ore belt, Baolun and Gezhen As-rich gold ore belt in the midwest of Hainan Island have contributed a large amount of As. Similarly, the higher value area of the coastal zone of Beihai City to Fangchenggang along Guangxi is associated closely with the over exploitation of As-rich mineral resources in Guangxi (Xiao et al., 2008).

In addition, the "spot-like" high-value areas of Pb concentration (>60 mg/kg) and Cu concentration are close to the heavy population, industrial and traffic developed district, and the high concentration of Pb and Cd could be caused by fossil fuel disposal or coal combustion in industry and transportation. Cu could come from discharge of wastewater (Neto et al., 2006), and long-term heavy usage of pesticides in agriculture (Nicholson et al., 2003). It is inferred that the higher value "spot" area of As, Pb and Cd concentrations at Xieyang Island may due to sample contamination because the inhabitants of Xieyang Island are mainly engaged in fishery and there is less industry activity.

4.2 *Provenance of heavy metals and its influencing factors at regional scale*

Spatial variations at regional scale remove the influence of local high-value variations, displaying distinctive directional feature, which could reveal the factor dominating the spatial distribution of heavy metals at regional scale.

At regional scale, Zn, Cr, Ni, Cu and Cd concentrations are dominated by parent rock materials from the Leizhou Peninsula and Hainan Island. Compared with granite exposed widely in the south of Guangxi, Quaternary basalt distributes extensively in the south and northeast of the Leizhou Peninsula, and north of Hainan Island, with more siderophile metals, such as Cu, Pb, Zn, Ni and so on. Meanwhile, Shilu iron-ore deposit, rich in metal minerals contained elements of Co, Cu and Ni, is another important source. The metals contained in rocks, are released as original crystal structure of the minerals broken during weathering process (Alloway, 1995), and enter the ocean with river. As concentration is dominated by parent rock materials from Hainan Island, secondly from the Leizhou Peninsula and Guangxi, and the Nandu River of Hainan Island is the main channel carrying source materials into the sea (Ma et al., 2010). The Nandu River originates in the places where locate the famous Shilu iron-ore deposits, Baolun and the Gezhen shear zone gold deposits as well as many small and medium-sized iron and gold ore deposits (spots) in drainage area (Liao et al., 2005). These deposits are associated with abundant As-rich minerals such as arsenopyrite (Ding et al., 2001). The high-value areas of As concentration from the Beihai Bay to Fangchenggang of Guangxi, attribute to the rich As-ore resource northwest of Guangxi Province (Xiao et al., 2008).

In addition, the materials coming from the South China Sea, i.e. the southeastern of the Beibu Gulf, the Red River in the west coast and the Pearl River materials through the Qiongzhou Strait (Dou et al., 2012; Tong et al., 2012; Li et al., 2012), made an important contribution to the Beibu Gulf.

The spatial distribution in WNW-NNW direction of heavy metals is mainly controlled by regional circulation of the Beibu Gulf. There exists a all year round large anticlockwise circulation in the Beibu Gulf (Fig. 2) (Sun, 2005; Chen et al., 2011) and the westward flow of Qiongzhou Strait, as well as the northward migration trend of sediments in the southwest and west side of Hainan Island (Xu, 2014; Xu et al., 2010), which dominate the direction of sediments migrating into the gulf. The materials derived from Guangxi land, the Leizhou Peninsula, Hainan Island and the Red River, the Qiongzhou Strait as well as the southeastern Beibu Gulf, migrate under the control of the ocean circulation, deposit in the "convergence center" as environmental conditions changes (Xu, 2014), forming the sedimentary pattern in NWW-NNW direction at regional scale.

The spatial distribution of As concentration, close to land in NNW direction, is different from other heavy metals, which might attribute to the different geochemical behavior. The migration of As depends mostly on the adsorption of colloidal Mn hydrous oxide (Ma et al., 1984; Liao, 1986) while Cu, Cr, Zn and Ni are mainly carried by clay particulates. This could be the main reason for not having obvious granularity effect in the distribution of As. Colloidal Mn hydrous oxide is prone to deposit in the coast area as the environment conditions change when plenty of sediments carried into the sea by the rivers and mixed with the sea water, while clay particulates could be transported a much longer distance because of their stable feature and the smaller size.

5 Conclusions

Factorial kriging was applied to the research on the spatial variations of the heavy metals in submarine, analyzing spatial multiscale structures, identifying and separating three-scale spatial variations of heavy metals. The spatial distribution of heavy metals at each scale could provide more geological significance-geological significance by removing spatial variations of other scales.

(1) There exist three-scale spatial structures consist of nugget effect, a spherical structure with range of 30 km, a spherical structure with range of 140 km. The spatial distribution of spherical structure with range of 30 km reflects the local-scale spatial variations of heavy metals, while the spatial distribution of spherical structure with range of 140 km represents the regional-scale spa-

tial variations.

(2) At local scale, Zn, Cr, Ni, Cu, Pb and Cd concentrations controlled by factor F_1, are derived mainly from parent rock materials of Hainan Island, the Leizhou Peninsula and Guangxi land, whose distribution are controlled by the granularity of sediments. As concentration, controlled by factor F_2, is dominated by anthropogenic pollution components from Hainan Island and the Leizhou Peninsula.

(3) At regional scale, Zn, Cr, Ni and Cu concentrations controlled by factor F_1, are derived primary from weathering of parent rock of the Leizhou Peninsula and Hainan Island, secondly from Guangxi land. As concentration, controlled by factor F_2, is derived mostly from Hainan Island, secondly from the Leizhou Peninsula and Guangxi land. The heavy metals are transported and migrated under the control of the anticlockwise circulation of the Beibu Gulf, and deposit in the “convergence center”, forming the distribution pattern in NWW-NNW direction.

(4) At regional scale, the spatial distribution of As concentration appears to be close to land in NNW direction compared with other metals, which attribute to their different loadings of migration in seawater, that As is mainly dependent on Mn and Fe hydrated oxide colloides, while Zn, Cr, Ni and Cu, are dependent on clay particulate materials.

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