ORIGINAL ARTICLE

Distribution, enrichment and sources of heavy metals in surface sediments of Hainan Island rivers, China

Debo Zhao[1,2] · Shiming Wan[1] · Zhaojie Yu[3] · Jie Huang[1]

Abstract Heavy metal concentrations in 36 samples of surface sediments from Hainan Island rivers were determined to evaluate the level of contamination in the region. Heavy metal concentrations (mg/kg) of Hainan Island rivers were in the range of 0.01–0.58 mg/kg for Hg, 0.09–0.70 mg/kg for Cd, 1.80–36.87 mg/kg for As, 15.33–69.32 mg/kg for Pb, 4.46–150.89 mg/kg for Cu, 6.64–104.95 mg/kg for Cr and 22.11–199.11 mg/kg for Zn. Contamination indices including contamination factor, enrichment factor, and geoaccumulation index, and multivariate statistical analyses indicated that Wenlan River was relatively at a considerable pollution level; Nandu, Changhua, Lingshui, Wanquan and Zhubi rivers were at a low-to-moderate pollution level; Beimen and Ningyuan rivers were at a level of relatively low pollution. Principal component analysis indicated that Cd, Pb, Cr and Zn were predominantly sourced from anthropogenic sources; whereas, Cu, As and Hg were from lithogenic sources. This study would be helpful for sustainable land use and marine management in the region.

Keywords Heavy metals · Hainan Island rivers · Surface sediment · Contamination indices · Multivariate statistical analyses · Sources

✉ Debo Zhao
zhao_debo123@163.com

[1] Key Laboratory of Marine Geology and Environment, Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China

[2] University of Chinese Academy of Sciences, Beijing 100049, China

[3] Laboratoire IDES, UMR 8148 CNRS, Université de Paris XI, 91405 Orsay, France

Introduction

Heavy metals have received huge concern due to its toxicity, non-biodegradable, wide sources and accumulative behaviors (Cooke et al. 1990; Irabien and Velasco 1999; Yu et al. 2008). Heavy metals discharged into an aquatic environment by natural or anthropogenic sources during their transport and a large quantity of free metal ions are deposited in sediments through adsorption, hydrolysis, and co-precipitation (Gaur et al. 2005). Heavy metal residues in sediments can affect water quality and thus accumulate in aquatic organisms, resulting in potential long-term damage on human health and the ecosystem (Ip et al. 2007; Raghunath et al. 1999). Therefore, sediments in an aquatic environment serve as an important reservoir for heavy metals and have attracted much attention of researchers (Dassenakis et al. 1997; Dou et al. 2013; Li et al. 2012; Singh et al. 2005).

Direct comparison of heavy metal concentration in sediments is an inappropriate way to assess the level of heavy metal pollution in sediments, because heavy metals originate from both crustal and anthropogenic sources and accumulate in sediments in the same manner (Idris 2008). Geochemical approaches such as the contamination factor (CF), enrichment factor (EF), and geoaccumulation index (Igeo) methods have been widely used to evaluate the impact of heavy metals in sediments (Chabukdhara and Nema 2012; Dou et al. 2013; Hu et al. 2013b; Varol 2011; Zhang et al. 2009). Multivariate statistical analysis approach, such as principal component analysis (PCA), factor analysis (FA) and cluster analysis (CA) are increasingly in use for environmental studies including measurement and monitoring of heavy metals in water and sediments (Facchinelli et al. 2001; Hu et al. 2013a; Loska and Wiechuła 2003; Varol 2011).
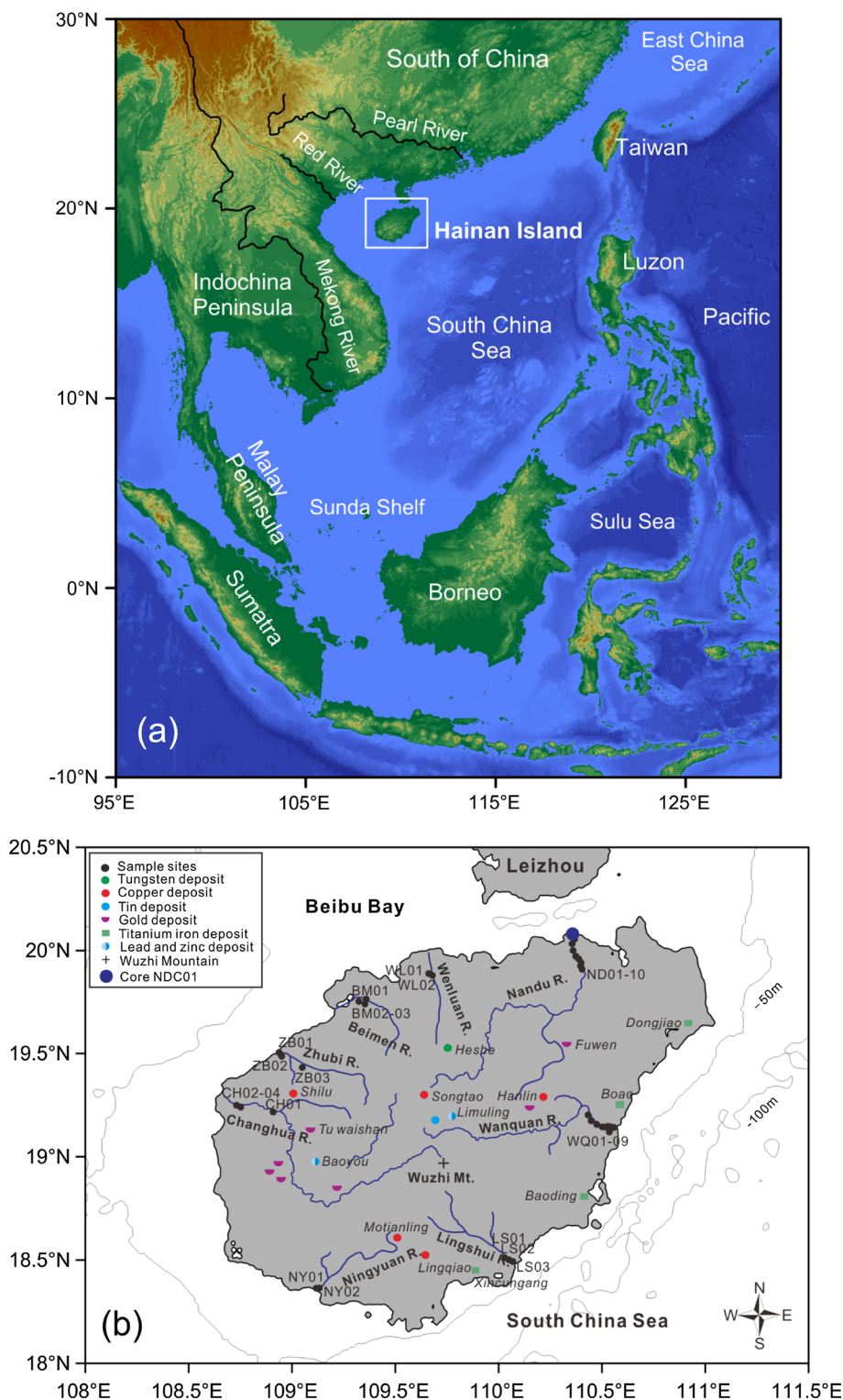
Fig. 1 Location of the study area and sampling sites. **a** The background map showing the studied area in Asia. **b** Map showing the river sampling sites, core NDC01, and main mines in the catchment of Hainan Island rivers

Hainan Island, located in the northern part of the South China Sea, and separated by the Qiongzhou Strait from the Leizhou Peninsula of Guangdong, is the second largest Island of China, with a surface area of 35.4×10^3 km^2 (Fig. 1a). Hainan Island is characterized by a radial river system, mostly originating from the central mountainous

area with high elevation. With rapid industrial and economic development on Hainan Island, these rivers may have been polluted to different degrees. Various studies on heavy metal contamination in river estuary and surrounding areas of the island have been conducted in recent years (Dou et al. 2013; Hu et al. 2013a). However, few studies

have focused on the sediments of the rivers of Hainan Island.

In this study, we firstly report the heavy metal concentration in sediments of major rivers in Hainan Island in order to (1) quantify the spatial distribution of heavy metals in surface sediments of eight rivers in Hainan Island; (2) assess the state of heavy metal contamination in the rivers using contamination indices; and (3) identify the possible sources of heavy metals via multivariate statistical analyses.

Geology and climate of study area

Tectonically, Hainan Island is located at the intersection of the Pacific oceanic plate, the Indochina Block and the southern margin of the South China Block (Metcalfe 2009). Late Paleozoic to Mesozoic granitoids and Cenozoic basalts dominate exposures on the island, with Proterozoic, Paleozoic, Mesozoic, and Cenozoic rocks preserved in isolated outcrops (Xu et al. 2014). Most of these granitoids are exposed in the central and southern parts of Hainan Island, and basalts are distributed in the northern part of Hainan Island (Fig. 2). Paleozoic–Mesozoic sedimentary rocks are widely developed in the west and scattered in the east Hainan Island. Paleozoic sedimentary rocks are shallow-marine strata and characterized by sandstone, slate, and limestone. In contrast, Mesozoic sedimentary rocks are terrestrial strata and characterized by volcanic-clastic rocks. Additionally, Quaternary sediments are widely distributed in the coastal plain around Hainan Island (Fu et al. 2000; Shi et al. 2011).

Hainan Island has a tropical moist monsoonal climate, and the topography is characterized by mountain in the central part, and hills and alluvial plains in the coastal areas. In terms of drainage area and mean discharge of the rivers in the island, the largest one is the Nandu River, which drains the central and northern parts of the island and flows northward to the Qiongzhou Strait (Fig. 1b). The second

largest one is the Changhua River, initialled at Wuzhi Mountain and flows westward through granite terrains and delivers the sediment to the Beibu Gulf. The third largest river is the Wanquan River, receiving the most abundant rainfall on the island and flowing eastward from the central mountains to the South China Sea. In addition, there are five moderate sized rivers named the Lingshui, Ningyuan, Zhubi, Beimen and Wenluan rivers on the island (Fig. 1b). There is limited knowledge about the suspended sediment yield for these rivers. According to Li (1992), rivers on the Hainan Island delivered about 4.0 million tons (Mt) solid sediments in total into the South China Sea annually, among which the Nandu, Changhua and Wanquan rivers contribute about 0.84, 0.52 and 0.52 Mt, respectively.

Materials and methods

A total of 36 surface sediment (0–5 cm) samples were collected in the lower reaches of eight rivers (Nandu, Wenlan, Beimen, Zhubi, Changhua, Ningyuan, Lingshui and Wanquan rivers) in Hainan Island using grab samplers in May 2013 (Fig. 1b). A 50-cm-long sediment core NDC01 (Fig. 1b) was recovered from the silt-rich mudflat in the Nandu River estuary using a hand-driven PVC coring pipe. At the laboratory, the river sediment samples and core samples were wet-sieved to remove >2 mm gravels and plant fragments and then air dried and ground into homogenous fine powder (Chabukdhara and Nema 2012).

Sediment subsamples (0.25 g) were digested in Teflon vessels with an acid mixture (5:4:1 HNO_3 + HCl + HF, in volume) (Loring and Rantala 1992) and then heated to 150° for 24 h on a heating plate. Afterwards, the solution was evaporated to dryness and extracted with HNO_3, adjusted to 40 g with double-deionized water. Heavy metals (As, Hg, Cd, Cr, Cu, Pb and Zn) were analyzed by ICP-AES. The interferences were corrected by the background correction and Interelement correction (IEC) methods (Sun et al. 2014). All the sediment samples were analyzed in duplicates and the quality assurance was guaranteed through the Blanks and China Stream Sediment Reference Materials (GBW07345, GSD9, and GSD4). The results were within the range of ±10 % of the certified values. The analytical precision is generally better than 1 % for major elements and 3 % for trace elements.

Grain-size measurements were carried out using a CILAS 940L apparatus to obtain the content of clay fraction particles. This facility can measure grains in the 0.3–2000 μm range, with a measurement repeatability of 0.5 %, and reproducibility better than 2 % (Wan et al. 2007). All the experiments were carried out in the Key Laboratory of Marine Geology and Environment, Institute of Oceanology, Chinese Academy of Sciences.
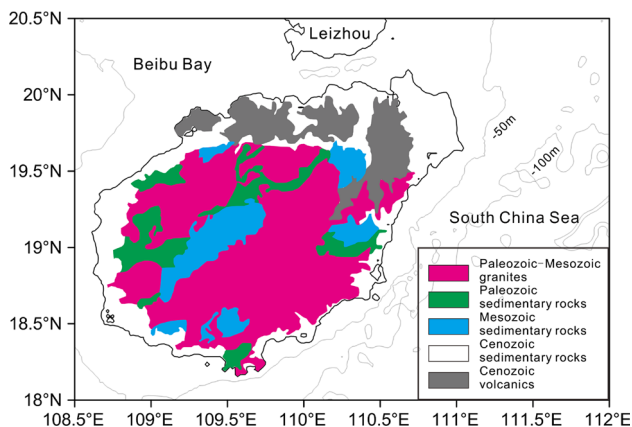

Fig. 2 Geological map (modified by Shi et al. 2011) of Hainan Island

Table 1 Heavy metal concentrations (mg/kg) in surface sediments of Hainan Island rivers

Sampling site	Hg (mg/kg)	Cd (mg/kg)	As (mg/kg)	Pb (mg/kg)	Cu (mg/kg)	Cr (mg/kg)	Zn (mg/kg)
BM01	0.035	0.226	9.83	48.8	32.4	62.2	93.7
BM02	0.032	0.291	4.70	30.6	22.5	36.8	56.7
BM03	0.020	0.127	2.34	25.2	9.08	23.3	25.5
WL01	0.013	0.612	7.56	44.8	60.3	105	199
WL02	0.577	0.402	6.40	37.9	72.6	87.5	159
ND01	0.015	0.530	7.68	52.8	33.6	76.8	114
ND02	0.027	0.456	11.5	57.2	37.9	97.5	135
ND03	0.043	0.233	8.97	35.8	25.2	58.8	84.1
ND04	0.036	0.158	3.56	23.3	13.7	30.4	41.4
ND05	0.038	0.126	3.32	26.8	12.1	21.8	42.4
ND06	0.019	0.558	10.56	50.1	30.7	74.3	110
ND07	0.071	0.412	14.9	69.3	39.5	105	157
ND08	0.022	0.440	6.31	33.7	24.4	63.3	82.4
ND09	0.011	0.309	5.72	32.2	16.9	50.0	60.1
ND10	0.007	0.701	5.45	44.6	35.1	80.8	113
CH01	0.046	0.288	23.0	44.9	57.9	21.7	69.7
CH02	0.026	0.336	16.7	54.9	52.4	33.0	90.2
CH03	0.075	0.394	36.9	62.2	151	40.7	116
CH04	0.039	0.294	19.3	51.1	35.9	42.5	139
LS01	0.025	0.397	3.60	53.1	31.1	65.2	137
LS02	0.015	0.327	2.15	50.0	22.1	56.6	128
LS03	0.020	0.358	3.04	50.1	23.0	57.5	113
NY01	0.022	0.133	3.91	23.3	13.5	15.6	48.0
NY02	0.026	0.085	1.80	15.3	4.46	6.64	22.1
WQ01	0.077	0.271	4.57	43.5	26.0	45.8	118
WQ02	0.045	0.391	3.64	42.2	27.5	56.8	104
WQ03	0.054	0.519	5.56	53.0	36.7	81.3	143
WQ04	0.020	0.436	9.65	64.7	39.6	90.7	168
WQ05	0.025	0.379	11.17	62.5	39.0	91.5	164
WQ06	0.032	0.414	4.71	45.0	23.5	60.2	102
WQ07	0.111	0.351	12.3	56.8	35.6	82.5	142
WQ08	0.051	0.177	4.81	33.9	15.6	36.2	65.0
WQ09	0.086	0.144	2.64	26.1	7.94	19.7	36.5
ZB01	0.013	0.101	6.10	26.1	15.5	23.5	60.2
ZB02	0.068	0.285	19.9	46.5	37.4	69.4	123
ZB03	0.041	0.397	12.2	45.4	39.0	63.3	113
Maximum	0.58	0.7	36.87	69.32	150.89	104.95	199.11
Minimum	0.01	0.09	1.8	15.33	4.46	6.64	22.11
Mean	0.05	0.33	8.79	43.44	33.35	56.48	102.1
S.D.	0.09	0.15	7.22	13.34	25.16	26.97	44.27

Results and discussion

Heavy metals in sediments of Hainan Island rivers

Concentrations and spatial distribution of heavy metals (As, Hg, Cd, Cr, Cu, Pb and Zn) in sediments of Hainan Island rivers are summarized in Table 1 and Fig. 3. The ranges of metals in sediments are: 0.01–0.58 mg/kg for Hg, 0.09–0.70 mg/kg for Cd, 1.80–36.87 mg/kg for As, 15.33–69.32 mg/kg for Pb, 4.46–150.89 mg/kg for Cu, 6.64–104.95 mg/kg for Cr, 22.11–199.11 mg/kg for Zn. The highest concentrations of Hg, Cr and Zn are found at Wenlan River, possibly due to metallic and industrial wastewater discharges from Heshe tungsten mine and
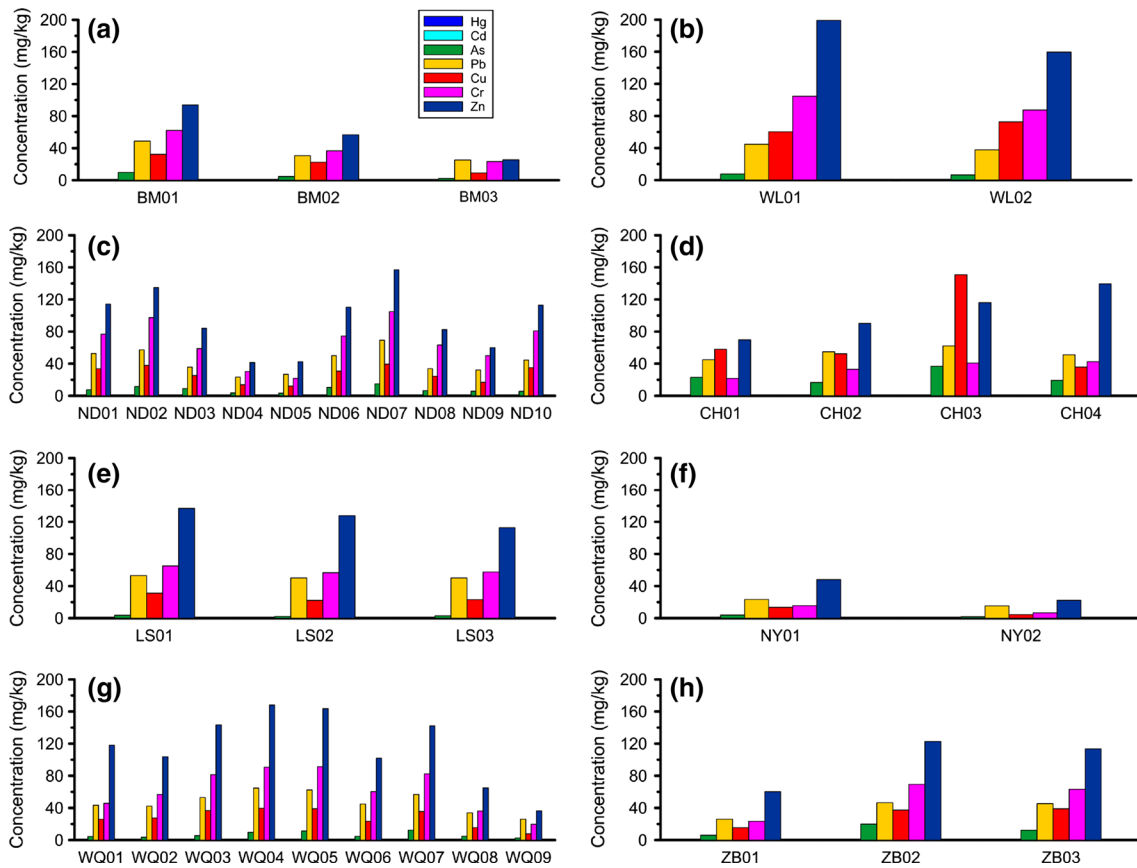
Fig. 3 Concentrations and spatial distribution of heavy metals in sediments of Hainan Island rivers. **a** Beimen River; **b** Wenlan River; **c** Nandu River; **d** Changhua River; **e** Lingshui River; **f** Ningyuan River; **g** Wanquan River; **h** Zhubi River

**Table 2** Summary of trace metal contents (mg/kg) in surface sediments of Hainan Island rivers and adjacent areas

Location	Hg	Cd	As	Pb	Cu	Cr	Zn	References
Mean concentration	0.05	0.33	8.79	43.44	33.35	56.48	102.10	This study
Beihai intertidal zone	0.07	0.22	9.08	16.60	12.71	–	–	Xia et al. (2008)
Eastern Beibu Bay	0.06	0.16	9.53	27.99	58.26	53.65	67.28	Dou et al. (2013)
Quanzhou Bay	0.4	0.59	21.7	67.7	71.4	82	179.6	Yu et al. (2008)
Changhua River estuary	0.02	0.09	9.51	27.0	15.0	53.1	73.7	Hu et al. (2013a)
Yangtze River estuary	0.04	0.20	11.6	21.9	28.0	52.1	78.0	An et al. (2010)
Pearl River estuary	0.33	5.60	33.1	105.9	81.0	118.1	140.0	Yang et al. (2009)
Primary standard, China	0.20	0.50	20.0	60.0	35.0	80.0	150.0	CSBTS (2002)

industrial area in the upper reaches of the river (Fig. 1b) (SBSM 2008). The metallic and industrial wastewater from the Hanlin gold and copper mine plants and industrial district in the upstream discharged into Nandu River, making Cd and Pb to reach the highest value. Changhua River receives metallic wastewater from Baoyou lead–zinc, Shilu copper and Tuwaishan gold mine plants in the upstream and middle reaches and thus has the highest As and Cu concentrations.

In this study, heavy metal concentrations of the river sediments from the Hainan Island were compared with adjacent areas (Table 2). The results show that the heavy metal concentrations in study area fall within the range of those of other regions listed. Most elements, including Hg (0.05 mg/kg), Cd (0.33 mg/kg), Pb (43.44 mg/g), Cu (33.35 mg/kg), Cr (56.48 mg/kg), and Zn (102.10 mg/kg), have relatively higher concentrations than those in Changhua River estuary (Hu et al. 2013a), but significantly lower than those of Quanzhou Bay (Yu et al. 2008). Concentrations of Hg and As (8.79 mg/kg) in this study are lower than those in Beihai intertidal zone (Xia et al. 2008) and Eastern Beibu Bay

Fig. 4 Frequency histograms and distribution curves of Cr and Pb (anthropogenic sources), and As and Cu (lithogenic sources)
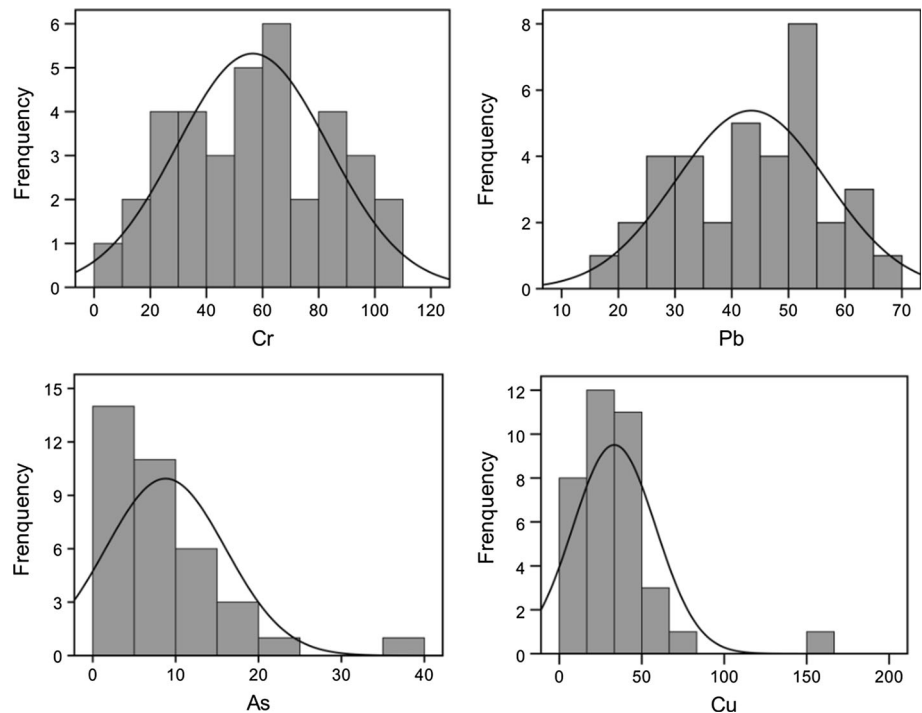
(Dou et al. 2013), but Cd, Pb, Cr and Zn have higher concentrations (Table 2). Compared with the national standard of marine sediment quality of China (GB 18668-2002) (CSBTS 2002), all the heavy metals in the Hainan Island rivers are characterized by much lower concentrations (Table 2).

In this work, the data of heavy metal concentration was tested with SPSS software, which suggested that the data followed a lognormal distribution. The frequency histograms and associated distribution curves for a lithogenic (As and Cu), and anthropogenic sources (Cr and Pb) are shown in Fig. 4. Some of the heavy metal concentrations show a wide variation as reflected by large standard deviation values. Due to these variations, mean concentration might be significantly affected by extremely high or low values. Median and/or geometric mean concentrations, on the other hand, will not be affected by these extreme values. Therefore, median concentrations of heavy metals are used for calculation in this study (Pekey 2006; Reimann et al. 2011).

Assessment of heavy metal pollution

Indication of contamination factor (CF)

Contamination factor is usually used to evaluate the pollution status of the environment by single substances (Hakanson 1980). This factor is calculated by dividing by background value:

$$CF = \frac{C_{Heavymetal}}{C_{Background}}. \tag{1}$$

Values of the contamination factor are characterized as follows: CF < 1 indicates low contamination; 1 < CF < 3 is moderate contamination; 3 < CF < 6 is considerable contamination; and CF > 6 is very high contamination (Hakanson 1980).

In most cases, it is difficult to determine the typical background of heavy metals for a given watershed due to the complex lithology and weathering features within the drainage areas (Audry et al. 2004; Zhang 1995). Moreover, it is essential to choose appropriate background values which are not influenced by anthropogenic process. Thus, the average element concentration values of 5 samples below 45 cm depth of Core NDC01 was regarded as not influenced by anthropogenic process and have been selected as a reference baseline.

The results of contamination factors (CFs) values are as follows (Table 3): Hg, 0.18–14.43 (median 0.80); Cd, 0.45–3.69 (median 1.81); As, 0.40–8.21 (median 1.38); Pb, 0.48–2.19 (median 1.42); Cu, 0.22–7.49 (median 1.53); Cr, 0.15–2.32 (median 1.29); Zn, 0.36–3.27 (median 1.83) (Table 3). The median CF value of Hg (0.80) is the lowest, indicating a "low contamination", while the median CF values of As (1.41), Cr (1.49), Cd (1.72), Zn (2.23), Pb (1.60), Cu (1.84), are less than 3.0, indicating a "moderate contamination". As shown in Fig. 5, Wenlan River has relatively high CF value, while Beimen and Ningyuan River have relatively low CF values, and the other five

Table 3 Metal contamination factors (CFs) for sediments of all sites studied in the Hainan Island rivers

| Sampling sites	Hg	Cd	As	Pb	Cu	Cr	Zn
BM01	0.88	1.19	2.19	1.54	1.61	1.37	1.54
BM02	0.80	1.53	1.05	0.97	1.12	0.81	0.93
BM03	0.50	0.67	0.52	0.80	0.45	0.52	0.42
WL01	0.33	3.22	1.68	1.41	2.99	2.31	3.27
WL02	14.43	2.11	1.43	1.19	3.60	1.93	2.62
ND01	0.38	2.79	1.71	1.66	1.67	1.70	1.88
ND02	0.68	2.40	2.57	1.80	1.88	2.16	2.22
ND03	1.08	1.23	2.00	1.13	1.25	1.30	1.38
ND04	0.90	0.83	0.79	0.73	0.68	0.67	0.68
ND05	0.95	0.66	0.74	0.85	0.60	0.48	0.70
ND06	0.48	2.94	2.35	1.58	1.53	1.64	1.81
ND07	1.78	2.17	3.31	2.19	1.96	2.32	2.58
ND08	0.55	2.32	1.41	1.06	1.21	1.40	1.36
ND09	0.28	1.63	1.27	1.02	0.84	1.11	0.99
ND10	0.18	3.69	1.21	1.41	1.74	1.79	1.86
CH01	1.15	1.52	5.12	1.42	2.88	0.48	1.15
CH02	0.65	1.77	3.71	1.73	2.60	0.73	1.48
CH03	1.88	2.07	8.21	1.96	7.49	0.90	1.91
CH04	0.98	1.55	4.29	1.61	1.78	0.94	2.29
LS01	0.63	2.09	0.80	1.67	1.54	1.44	2.25
LS02	0.38	1.72	0.48	1.58	1.09	1.25	2.10
LS03	0.50	1.88	0.68	1.58	1.14	1.27	1.85
NY01	0.55	0.70	0.87	0.73	0.67	0.34	0.79
NY02	0.65	0.45	0.40	0.48	0.22	0.15	0.36
WQ01	1.93	1.43	1.02	1.37	1.29	1.01	1.94
WQ02	1.13	2.06	0.81	1.33	1.36	1.25	1.71
WQ03	1.35	2.73	1.24	1.67	1.82	1.80	2.36
WQ04	0.50	2.29	2.15	2.04	1.97	2.01	2.77
WQ05	0.63	2.00	2.49	1.97	1.94	2.02	2.69
WQ06	0.80	2.18	1.05	1.42	1.17	1.33	1.68
WQ07	2.78	1.85	2.74	1.79	1.77	1.82	2.34
WQ08	1.28	0.93	1.07	1.07	0.77	0.80	1.07
WQ09	2.15	0.76	0.59	0.82	0.39	0.43	0.60
ZB01	0.33	0.53	1.36	0.82	0.77	0.52	0.99
ZB02	1.70	1.50	4.42	1.46	1.86	1.53	2.02
ZB03	1.03	2.09	2.72	1.43	1.94	1.40	1.87
Min	0.18	0.45	0.40	0.48	0.22	0.15	0.36
Max	14.43	3.69	8.21	2.19	7.49	2.32	3.27
Median	0.80	1.81	1.38	1.42	1.53	1.29	1.83

rivers fall in moderate level. Most mean CF values are less than 3.0, which indicates a low-to-moderate contamination. Generally, mean CF values of Hainan Island rivers are higher than Yangtze River estuary (An et al. 2010), and lower than Pearl River estuary (Yang et al. 2009).

Indication of enrichment factor (EF)

Enrichment factor is a useful tool to discriminate between natural and anthropogenic sources and to reflect the status of heavy metal pollution (Sakan et al. 2009). In a closed system, the mobility, transport and fractionation of heavy metals are a function of the chemical form of the element, which, in turn, is controlled by the physicochemical and biological characteristics of the system (Bacon and Davidson 2008). The water-soluble heavy metal elements were readily absorbed by fine particle fraction of river sediments, such as hydrated oxides of iron and manganese, organic compound and clay minerals (Sakan et al. 2009). In order to eliminate the influence of grain size and mineral

Fig. 5 Contamination factor (CF) of heavy metals in the surface sediments of Hainan Island rivers, Yangtze River and Pearl River. Background of Al of Yangtze River and Pearl River from Yang and Li (1999) and Peng et al. (2003), respectively. The *dotted lines* represent the level of CF (Hakanson 1980)
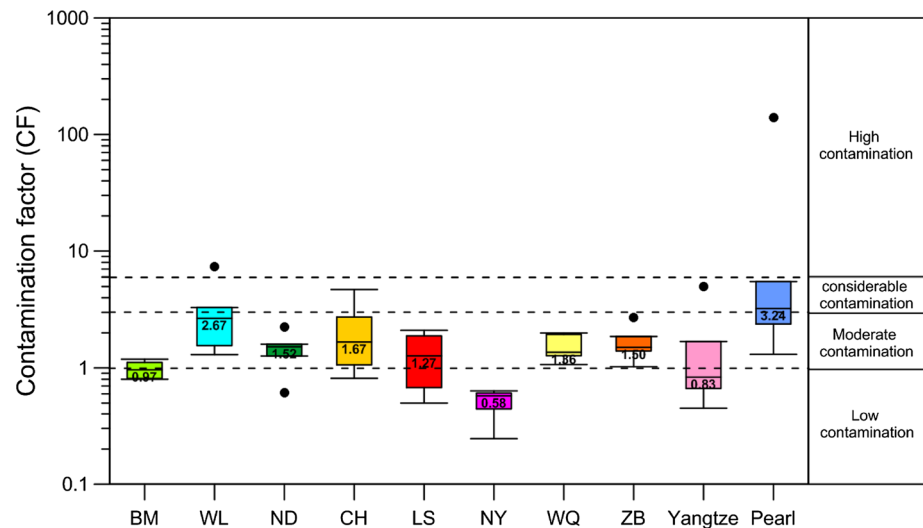
composition on elemental concentrations and alleviate the variations produced by physicochemical processes of the heterogeneous sediments and crustal rocks, heavy metal concentrations are generally normalized by conservative elements, such as Al, Fe, Sc (Amin et al. 2009; Bhuiyan et al. 2011; Meza-Figueroa et al. 2009; Pekey 2006). In this study, heavy metals and Al average concentration of 5 samples below 45 cm depth of core NDC01 were used as the background values. EF is calculated using the following equation:

$$EF = \frac{(Me/Al)_{Sample}}{(Me/Al)_{Background}}, \qquad (2)$$

where $(Me/Al)_{Sample}$ and $(Me/Al)_{Background}$ are the ratios of concentration of metals to Al of samples and background references. EF values were interpreted as follows: EF < 1 indicates no enrichment; 1–3 is minor enrichment; 3–5 is moderate enrichment; 5–10 is moderately severe enrichment; 10–25 is severe enrichment; 25–50 is very severe enrichment; and >50 is extremely severe enrichment (Sakan et al. 2009).

The EF ranges of the heavy metals of Hainan Island rivers sediments are as follows (Table 4): Hg 0.15–12.43 (median 0.69); Cd 1.01–8.29 (median 4.06); As 1.09–22.24 (median 3.74); Pb 1.09–4.92 (median 3.19); Cu 0.38–12.73 (median 2.61); Cr 0.23–3.62 (median 2.00); Zn 0.51–4.62 (median 2.59) (Table 4). The median EF values of Cu, Cr and Zn are between 1 and 3, indicating a "minor enrichment", while Hg is less than 1, suggesting "no enrichment". The median EF values of Cd, As and Pb are higher than 3, indicating "moderate enrichment". The low EF values (0.5–1.5) indicate that the metal is entirely from crustal materials or natural processes, while higher EF values than 1.5 suggest a significant contribution of

noncrustal materials to the trace metals (Zhang and Liu 2002). In this study, the median EF values for almost all metals except Hg were >1.5 in the sediments of the rivers, suggesting a significant anthropogenic impact on the metal levels in the rivers. Specifically, Wenlan River has relatively high EF value (Fig. 6), while Beimen and Ningyuan rivers have relatively low EF value, and the other five rivers fall in their moderate level. Most median EF values of the rivers are less than 5.0, suggesting no enrichment to moderate enrichment. In general, median EF values of Hainan Island rivers are higher than Yangtze River estuary, and lower than Pearl River estuary.

Geoaccumulation index (Igeo)

Geoaccumulation index is basically a single metal approach to quantify metal pollution in sediments and defined by the following equation:

$$Igeo = \log_2(Cn/(1.5 \times Bn)), \qquad (3)$$

where Cn is the measured concentration of the examined metal (*n*) in the sediment and Bn is the geochemical background concentration of the metal (*n*), the average element concentration values of 5 samples below 45 cm depth of Core NDC01 were used as the background values. Factor 1.5 is the background matrix correction factor due to lithogenic effects (Müller 1979). Müller has distinguished seven classes of geoaccumulation index (Müller 1981). Class 0 (practically unpolluted), Igeo ≤ 0; Class 1 (unpolluted to moderately polluted), 0 < Igeo < 1; Class 2 (moderately polluted), 1 < Igeo < 2; Class 3 (moderately to heavily polluted), 2 < Igeo < 3; Class 4 (heavily polluted), 3 < Igeo < 4; Class 5 (heavily to extremely polluted): 4 < Igeo < 5; Class 6 (extremely polluted), Igeo > 5.

Table 4 Enrichment factors (EFs) for sediments of all sites studied in the Hainan Island rivers

Sampling site	Hg	Cd	As	Pb	Cu	Cr	Zn
BM01	0.75	2.67	5.93	3.46	2.73	2.14	2.17
BM02	0.69	3.44	2.84	2.17	1.90	1.27	1.31
BM03	0.43	1.50	1.41	1.79	0.77	0.80	0.59
WL01	0.28	7.24	4.56	3.18	5.08	3.60	4.62
WL02	12.43	4.75	3.86	2.69	6.12	3.01	3.70
ND01	0.32	6.27	4.63	3.75	2.84	2.65	2.65
ND02	0.58	5.39	6.95	4.06	3.19	3.36	3.13
ND03	0.93	2.76	5.41	2.54	2.13	2.03	1.95
ND04	0.78	1.87	2.15	1.65	1.15	1.05	0.96
ND05	0.82	1.49	2.00	1.90	1.02	0.75	0.98
ND06	0.41	6.60	6.37	3.55	2.59	2.56	2.56
ND07	1.53	4.88	8.97	4.92	3.33	3.62	3.64
ND08	0.47	5.20	3.81	2.39	2.06	2.18	1.91
ND09	0.24	3.65	3.45	2.29	1.43	1.72	1.39
ND10	0.15	8.29	3.29	3.16	2.96	2.79	2.62
CH01	0.99	3.41	13.86	3.19	4.89	0.75	1.62
CH02	0.56	3.97	10.05	3.89	4.42	1.14	2.09
CH03	1.62	4.65	22.24	4.42	12.73	1.40	2.69
CH04	0.84	3.48	11.62	3.62	3.03	1.46	3.23
LS01	0.54	4.70	2.17	3.77	2.62	2.25	3.17
LS02	0.32	3.87	1.30	3.55	1.86	1.95	2.96
LS03	0.43	4.23	1.83	3.55	1.94	1.98	2.62
NY01	0.47	1.57	2.36	1.65	1.14	0.54	1.11
NY02	0.56	1.01	1.09	1.09	0.38	0.23	0.51
WQ01	1.66	3.21	2.76	3.08	2.19	1.58	2.74
WQ02	0.97	4.62	2.20	3.00	2.32	1.96	2.41
WQ03	1.16	6.14	3.35	3.76	3.10	2.80	3.33
WQ04	0.43	5.15	5.82	4.59	3.34	3.13	3.90
WQ05	0.54	4.48	6.74	4.43	3.29	3.15	3.79
WQ06	0.69	4.89	2.84	3.19	1.98	2.08	2.36
WQ07	2.39	4.15	7.42	4.03	3.00	2.84	3.30
WQ08	1.10	2.10	2.90	2.40	1.31	1.25	1.51
WQ09	1.85	1.71	1.59	1.86	0.67	0.68	0.85
ZB01	0.28	1.19	3.68	1.85	1.31	0.81	1.40
ZB02	1.46	3.37	11.98	3.30	3.15	2.39	2.85
ZB03	0.88	4.70	7.35	3.22	3.29	2.18	2.63
Min	0.15	1.01	1.09	1.09	0.38	0.23	0.51
Max	12.43	8.29	22.24	4.92	12.73	3.62	4.62
Median	0.69	4.06	3.74	3.19	2.61	2.00	2.59

The calculated Igeo values of heavy metals are as follows (Table 5): Hg −3.10 to 3.27 (median −0.91); Cd −1.75 to 1.30 (median 0.27); As −1.90 to 2.45 (median −0.12); Pb −1.63 to 0.54 (median −0.08); Cu −2.76 to 2.32 (median 0.03); Cr −3.35 to 0.63 (median −0.22); Zn −2.04 to 1.13 (median 0.29). The median Igeo of Hg, As, Pb and Cr are less than zero (Igeo < 0), suggesting that the Hainan Island rivers have not been polluted overall by these metals. In contrast, median Igeo values of Cd, Cu and Zn are all between 0 and 1, indicating that these rivers are in the level of "unpolluted to moderately polluted". Among the eight major rivers of Hainan Island, Wenlan has relatively high Igeo value (Fig. 7), Beimen and Ningyuan rivers have relatively low Igeo value, the other 5 rivers
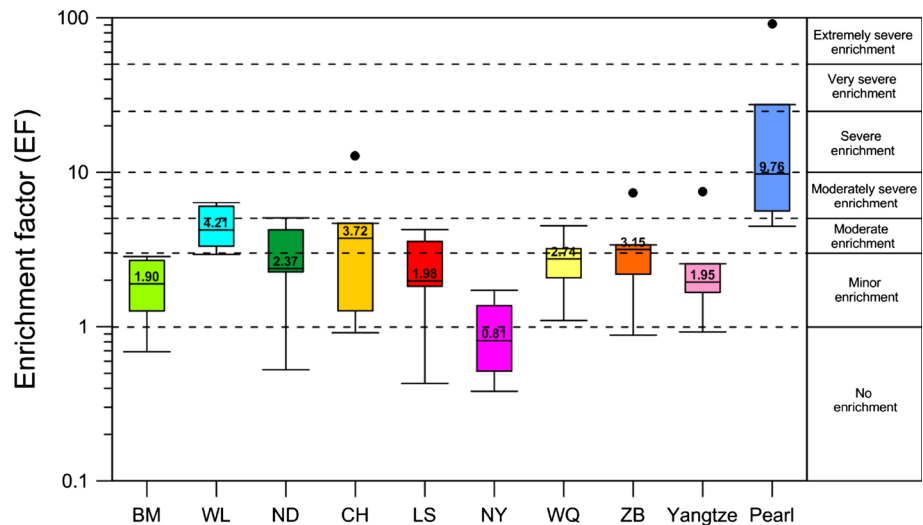
have moderate values. All the rivers' median Igeo values are <2, indicating unpolluted to moderately polluted level. In general, median Igeo values of Hainan Island rivers are higher than Yangtze River estuary, and lower than Pearl River estuary.

In summary, the major rivers of Hainan Island are in the level of unpolluted to considerable polluted status based on multiple evaluation indexes including CF, EF and Igeo (Figs. 5, 6, 7). Specifically, Wenlan River is relatively at a high pollution level, which is at a moderate to considerable level. Nandu, Changhua, Lingshui, Wanquan and Zhubi rivers are at a low-to-moderate pollution level. Beimen and Ningyuan rivers are at a level of relatively low pollution. Compared with Chinese large rivers, the pollution level of Hainan Island rivers is lower than Pearl River estuary, but higher than Yangtze River estuary.

Heavy metals sources

Principal component analysis (PCA)

In order to extract dominant factors of spatial variations of heavy metals, PCA of heavy metal concentration and clay contents in river sediments of Hainan Island was performed. The rotated component matrixes of the PCA are presented in Table 6. The loading plot of the first two principal components of the samples is depicted in Fig. 8. The results indicate that the variability of heavy metals can be expressed by two principal components that together explain 66.9 % of the total variance.

The first principal component (PC1), accounting for 49.1 % of the total variance, has high loadings of Cd, Pb, Cr and Zn. This suggests that these metals may have similar sources of natural and/or anthropogenic origins. The second component (PC2), explaining 17.8 % of the total variance,

has relatively high loadings on As, Hg, Cu and clay contents. The fine clay particles play an important role to carry trace metals in rivers (Ip et al. 2007), thus we can conclude that As, Hg and Cu are from lithogenic sources. The main anthropogenic source for heavy metals can be the direct discharges of waste water with metal contaminants from local industrial and urban. Such industrial sources in Hainan Island may include the tungsten mine, gold mine, copper mine and lead–zinc deposits. In addition, preliminary studies argued that the distributions of Cd are closely related to the intensive use of phosphate fertilizers (Xia et al. 2011; Zhang and Shan 2008). Therefore, we suggest that Cd, Pb, Cr, Zn in Hainan River sediments originated primarily from anthropogenic sources based on the evidence of a large number of mineral deposits and agricultural development in the river basins of Hainan Island.

Cluster analysis

Cluster analysis (CA) was also applied to the river sediment quality data set to identify the rivers with similar pollution level. The CA dendrogram (Fig. 9) shows that the eight rivers can be grouped into three statistically significant clusters. Cluster 1 (Wenlan River) is at a relatively high pollution level. Cluster 2 (Nandu, Changhua, Lingshui, Wanquan and Zhubi rivers) is at a moderate pollution level. Cluster 3 (Beimen and Ningyuan rivers) is at a level of relatively low pollution.

Wenlan River is located in the northern Hainan Island characterized by low altitude and flat terrain. The long residence time of water and sediment, high population density and widely distributed mining and industry in this area together result in high pollution of the river. Beimen and Ningyuan river basins have only a very few mines, which maybe the main reason of relatively low pollution

Table 5 Geoaccumulation index (Igeo) for sediments of all sites studied in the Hainan Island rivers

Sampling sites	Hg	Cd	As	Pb	Cu	Cr	Zn
BM01	−0.78	−0.33	0.55	0.04	0.10	−0.13	0.04
BM02	−0.91	0.03	−0.52	−0.64	−0.43	−0.88	−0.69
BM03	−1.58	−1.17	−1.52	−0.91	−1.74	−1.54	−1.84
WL01	−2.21	1.10	0.17	−0.09	1.00	0.62	1.13
WL02	3.27	0.50	−0.07	−0.33	1.26	0.37	0.81
ND01	−2.00	0.90	0.19	0.15	0.15	0.18	0.32
ND02	−1.15	0.68	0.78	0.27	0.33	0.52	0.56
ND03	−0.48	−0.29	0.41	−0.41	−0.26	−0.21	−0.12
ND04	−0.74	−0.85	−0.92	−1.03	−1.14	−1.16	−1.14
ND05	−0.66	−1.18	−1.02	−0.83	−1.32	−1.64	−1.11
ND06	−1.66	0.97	0.65	0.07	0.02	0.13	0.27
ND07	0.24	0.53	1.14	0.54	0.38	0.63	0.78
ND08	−1.45	0.63	−0.09	−0.50	−0.31	−0.10	−0.15
ND09	−2.45	0.12	−0.24	−0.56	−0.84	−0.44	−0.60
ND10	−3.10	1.30	−0.31	−0.09	0.22	0.25	0.31
CH01	−0.38	0.02	1.77	−0.08	0.94	−1.65	−0.39
CH02	−1.21	0.24	1.31	0.21	0.79	−1.04	−0.02
CH03	0.32	0.47	2.45	0.39	2.32	−0.74	0.35
CH04	−0.62	0.04	1.52	0.10	0.25	−0.68	0.61
LS01	−1.26	0.48	−0.90	0.16	0.04	−0.06	0.58
LS02	−2.00	0.20	−1.65	0.07	−0.45	−0.26	0.49
LS03	−1.58	0.33	−1.15	0.07	−0.39	−0.24	0.31
NY01	−1.45	−1.10	−0.79	−1.03	−1.16	−2.12	−0.93
NY02	−1.21	−1.75	−1.90	−1.63	−2.76	−3.35	−2.04
WQ01	0.36	−0.07	−0.56	−0.13	−0.22	−0.57	0.37
WQ02	−0.42	0.46	−0.89	−0.17	−0.14	−0.26	0.19
WQ03	−0.15	0.86	−0.28	0.16	0.28	0.26	0.65
WQ04	−1.58	0.61	0.52	0.44	0.39	0.42	0.88
WQ05	−1.26	0.41	0.73	0.39	0.37	0.43	0.84
WQ06	−0.91	0.54	−0.52	−0.08	−0.36	−0.17	0.16
WQ07	0.89	0.30	0.87	0.26	0.24	0.28	0.64
WQ08	−0.23	−0.68	−0.49	−0.49	−0.96	−0.91	−0.49
WQ09	0.52	−0.98	−1.35	−0.86	−1.93	−1.79	−1.32
ZB01	−2.21	−1.50	−0.14	−0.87	−0.96	−1.53	−0.60
ZB02	0.18	0.00	1.56	−0.03	0.31	0.03	0.43
ZB03	−0.55	0.48	0.86	−0.07	0.37	−0.10	0.32
Min	−3.10	−1.75	−1.90	−1.63	−2.76	−3.35	−2.04
Max	3.27	1.30	2.45	0.54	2.32	0.63	1.13
Median	−0.91	0.27	−0.12	−0.08	0.03	−0.22	0.29

level. In contrast, Changhua, Wanquan, Lingshui and Zhubi rivers are all typical mountainous rivers, which have a lower water-storage capacity and a quicker response to short precipitation episodes. Nandu River has the largest catchment areas and water volume. Therefore, these rivers can transport significant sedimentary loads with associated pollutants in short periods of time, which place them at a moderate pollution level.

Conclusions

Several heavy metals in the surface sediments of the major rivers of Hainan Island were evaluated by different assessment methods, including contamination factor (CF), enrichment factor (EF), geoaccumulation index (Igeo), PCA, and cluster analysis (CA). Wenlan River has the highest concentrations of Hg, Cr and Zn; Nandu River have

Fig. 7 Geoaccumulation index (Igeo) of heavy metals in the surface sediments of Hainan Island rivers, Yangtze River and Pearl River. Background of Al of Yangtze River and Pearl River from Yang and Li (1999) and Peng et al. (2003), respectively. The *dotted lines* represent the level of Igeo (Müller 1981)
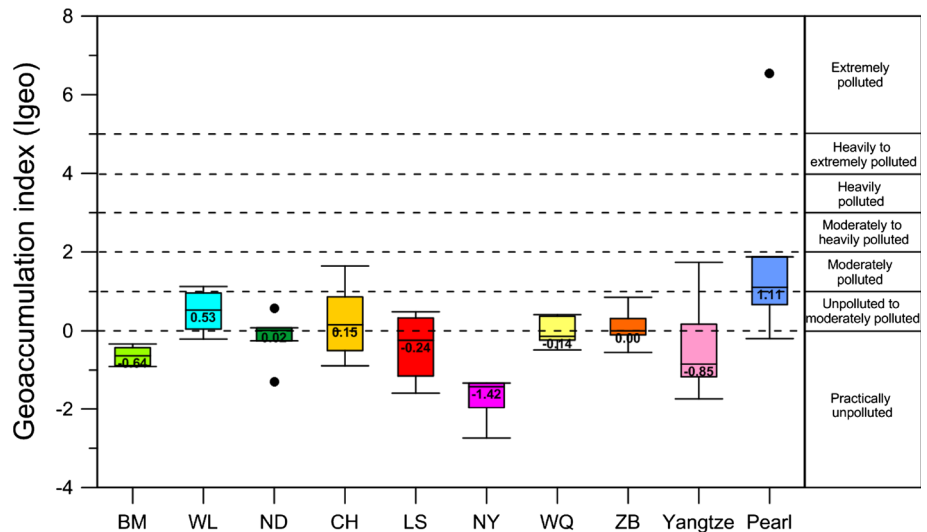

Table 6 The rotated component matrixes of heavy metals in sediments of Hainan Island rivers

Elements	Component	
	1	2
Hg	0.23	0.22
Cd	0.79	−0.39
As	0.55	0.75
Pb	0.90	−0.02
Cu	0.71	0.62
Cr	0.84	−0.47
Zn	0.92	−0.24
Clay	0.30	0.12
Total variance %	49.09	17.83
Cumulative % variance %	49.09	66.92

Extraction method: principal component analysis
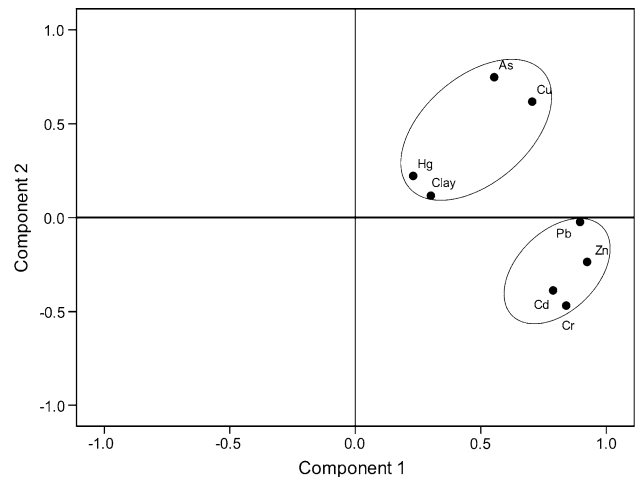
Fig. 8 Principal component analysis (PCA) loading plot of heavy metal concentrations and clay contents in the sediments

the highest values of Cd and Pb; and Changhua River has the highest values of As and Cu.

Based on the variations of CF, EF and Igeo, Hainan Island rivers are in the level of unpolluted to considerable polluted; Wenlan River is relatively at a moderate to considerable pollution level; Nandu, Changhua, Lingshui, Wanquan and Zhubi rivers are at a low-to-moderate pollution level; Beimen and Ningyuan River are at a level of relatively low pollution.

According to PCA, two different source models exist in the sediments. Cd, Pb, Cr and Zn are predominantly originated from anthropogenic sources; whereas, Cu, As
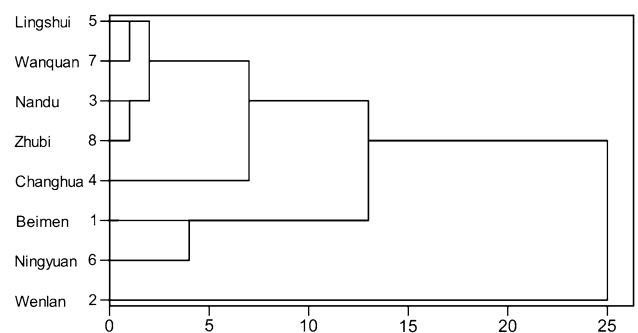

Fig. 9 Dendrogram showing clustering of heavy metal contents from each river sediments

and Hg from lithogenic sources. Cluster analysis (CA) grouped eight rivers into three statistically significant clusters. Wenlan river is relatively at a high pollution level. Nandu, Changhua, Lingshui, Wanquan and Zhubi rivers are at a moderate pollution level. Beimen and Ningyuan rivers are at a level of relatively low pollution. Natural factors including topography, mines distribution, river catchment areas and water volume, and anthropogenic factors including mining, industrial and the local residents discharge waste caused different heavy metal enrichment levels in these rivers.

References

Amin B, Ismail A, Arshad A, Yap CK, Kamarudin MS (2009) Anthropogenic impacts on heavy metal concentrations in the coastal sediments of Dumai, Indonesia. Environ Monit Assess 148:291–305

An Q, Wu Y, Wang J, Li Z (2010) Assessment of dissolved heavy metal in the Yangtze river estuary and its adjacent sea, China. Environ Monit Assess 164:173–187

Audry S, Schafer J, Blanc G, Jouanneau JM (2004) Fifty-year sedimentary record of heavy metal pollution (Cd, Zn, Cu, Pb) in the Lot river reservoirs (France). Environ Pollut 132:413–426

Bacon JR, Davidson CM (2008) Is there a future for sequential chemical extraction? Analyst 133:25–46

Bhuiyan MA, Suruvi NI, Dampare SB, Islam MA, Quraishi SB, Ganyaglo S, Suzuki S (2011) Investigation of the possible sources of heavy metal contamination in lagoon and canal water in the tannery industrial area in Dhaka, Bangladesh. Environ Monit Assess 175:633–649

Chabukdhara M, Nema AK (2012) Assessment of heavy metal contamination in Hindon River sediments: a chemometric and geochemical approach. Chemosphere 87:945–953

Cooke JA, Andrews SM, Johnson MS (1990) Lead, zinc, cadmium and fluoride in small mammals from contaminated grassland established on fluorspar tailings. Water Air Soil Pollut 51:43–54

CSBTS (2002) The People's Republic of China National Standards GB 18668-2002-Marine Sediment Quality. China State Bureau of Quality and Technical Supervision: 10

Dassenakis M, Scoullos M, Gaitis A (1997) Trace metals transport and behaviour in the Mediterranean estuary of Acheloos River. Mar Pollut Bull 34:103–111

Dou Y, Li J, Zhao J, Hu B, Yang S (2013) Distribution, enrichment and source of heavy metals in surface sediments of the eastern Beibu Bay, South China Sea. Mar Pollut Bull 67:137–145

Facchinelli A, Sacchi E, Mallen L (2001) Multivariate statistical and GIS-based approach to identify heavy metal sources in soils. Environ Pollut 114:313–324

Fu G, Li M, Zeng W (2000) Geology in Hainan Island. Chinese Geology Press, New York

Gaur VK, Gupta SK, Pandey SD, Gopal K, Misra V (2005) Distribution of heavy metals in sediment and water of river Gomti. Environ Monit Assess 102:419–433

Hakanson L (1980) An ecological risk index for aquatic pollution control. A sedimentological approach. Water Res 14:975–1001

Hu B, Cui R, Li J, Wei H, Zhao J, Bai F, Song W, Ding X (2013a) Occurrence and distribution of heavy metals in surface sediments of the Changhua river estuary and adjacent shelf (Hainan Island). Mar Pollut Bull 76:400–405

Hu B, Li G, Li J, Bi J, Zhao J, Bu R (2013b) Spatial distribution and ecotoxicological risk assessment of heavy metals in surface sediments of the southern Bohai Bay, China. Environ Sci Pollut Res Int 20:4099–4110

Idris AM (2008) Combining multivariate analysis and geochemical approaches for assessing heavy metal level in sediments from Sudanese harbors along the Red Sea coast. Microchem J 90:159–163

Ip CC, Li XD, Zhang G, Wai OW, Li YS (2007) Trace metal distribution in sediments of the Pearl river estuary and the surrounding coastal area, South China. Environ Pollut 147:311–323

Irabien MJ, Velasco F (1999) Heavy metals in Oka river sediments (Urdaibai National Biosphere Reserve, northern Spain): lithogenic and anthropogenic effects. Environ Geol 37:54–63

Li L (1992) Hydrological character in Hainan island. Hydrology 6:49–51

Li X, Liu L, Wang Y, Luo G, Chen X, Yang X, Gao B, He X (2012) Integrated assessment of heavy metal contamination in sediments from a coastal industrial basin, NE China. PloS one 7:e39690

Loring D, Rantala R (1992) Manual for the geochemical analyses of marine sediments and suspended particulate matter. Earth Sci Rev 32:235–283

Loska K, Wiechuła D (2003) Application of principal component analysis for the estimation of source of heavy metal contamination in surface sediments from the Rybnik reservoir. Chemosphere 51:723–733

Metcalfe I (2009) Late Palaeozoic and Mesozoic tectonic and palaeogeographical evolution of SE Asia. Geol Soc Lond (Spec Publ) 315:7–23

Meza-Figueroa D, Maier RM, de la O-Villanueva M, Gomez-Alvarez A, Moreno-Zazueta A, Rivera J, Campillo A, Grandlic CJ, Anaya R, Palafox-Reyes J (2009) The impact of unconfined mine tailings in residential areas from a mining town in a semi-arid environment: Nacozari, Sonora, Mexico. Chemosphere 77:140–147

Müller G (1979) Schwermetalle in den Sedimenten des Rheins-Veränderungen seit 1971. Umschau 79:778–783

Müller G (1981) Die Schwermetallbelastung der sedimente des Neckars und seiner Nebenflusse: eine Bestandsaufnahme. Chem Zeitung 105:157–164

Pekey H (2006) The distribution and sources of heavy metals in Izmit Bay surface sediments affected by a polluted stream. Mar Pollut Bull 52:1197–1208

Peng X, Zhou H, Weng H, Pan J, Chen G (2003) Characteristics of major elements' constitutions and distributions in sediments of the Lingdingyang in the Pearl River Estuary and their geochemical implication. J Zhejiang Univ (Science Edition) 30:697–702 (in Chinese with English abstract)

Raghunath R, Tripathi RM, Kumar AV, Sathe AP, Khandekar RN, Nambi KS (1999) Assessment of Pb, Cd, Cu, and Zn exposures of 6- to 10-year-old children in Mumbai. Environ Res 80:215–221

Reimann C, Filzmoser P, Garrett R, Dutter R (2011) Statistical data analysis explained: applied environmental statistics with R. John Wiley & Sons, Chichester

Sakan SM, Dordevic DS, Manojlovic DD, Predrag PS (2009) Assessment of heavy metal pollutants accumulation in the Tisza river sediments. J Environ Manage 90:3382–3390

SBSM (2008) Electronic atlas of Hainan province. The state bureau of surveying and mapping in Hainan data information center

Shi X, Kohn B, Spencer S, Guo X, Li Y, Yang X, Shi H, Gleadow A (2011) Cenozoic denudation history of southern Hainan Island, South China Sea: constraints from low temperature thermochronology. Tectonophysics 504:100–115

Singh KP, Malik A, Sinha S (2005) Water quality assessment and apportionment of pollution sources of Gomti river (India) using multivariate statistical techniques—a case study. Anal Chim Acta 538:355–374

Sun S, Song X, Sun Y, Ma X, Li J, Chen J, Huang T, Cao L (2014) Determination of multiple metallic elements in oceanic sediments by ICP-AES. Chin J Inorg Anal Chem 4:35–38

Varol M (2011) Assessment of heavy metal contamination in sediments of the Tigris river (Turkey) using pollution indices and multivariate statistical techniques. J Hazard Mater 195:355–364

Wan S, Li A, Clift PD, Stuut J-BW (2007) Development of the east Asian monsoon: mineralogical and sedimentologic records in the northern south China Sea since 20 Ma. Palaeogeogr Palaeoclimatol Palaeoecol 254:561–582

Xia P, Meng X, Yin P, Liu L (2008) Heavy metal pollution and its potential ecological risk in the sediments from the Beihai intertidal zone of Guangxi province. Adv Mar Sci 26:471–477

Xia P, Meng X, Yin P, Cao Z, Wang X (2011) Eighty-year sedimentary record of heavy metal inputs in the intertidal sediments from the Nanliu river estuary, Beibu Gulf of South China Sea. Environ Pollut 159:92–99

Xu Y, Cawood PA, Du Y, Zhong Z, Hughes NC (2014) Terminal suturing of Gondwana along the southern margin of South China Craton: evidence from detrital zircon U-Pb ages and Hf isotopes in Cambrian and Ordovician strata, Hainan island. Tectonics 33:2490–2504

Yang S, Li C (1999) Characteristic element compositions of the Yangtze and the Yellow River sediments and their geological background. Mar Geol Quat Geol 19:19–26 (in Chinese with English abstract)

Yang W, Lai Z, Wei T (2009) Pollution and ecological hazard evaluation of sediment heavy metals in Pearl River Estuary. J Zhejiang Ocean Univ (Natural Science) 2:188–232 (in Chinese with English abstract)

Yu R, Yuan X, Zhao Y, Hu G, Tu X (2008) Heavy metal pollution in intertidal sediments from Quanzhou Bay, China. J Environ Sci 20:664–669

Zhang J (1995) Geochemistry of trace metals from Chinese river/estuary systems: an overview. Estuar Coast Shelf Sci 41:631–658

Zhang J, Liu C (2002) Riverine composition and estuarine geochemistry of particulate metals in China—weathering features, anthropogenic impact and chemical fluxes. Estuar Coast Shelf Sci 54:1051–1070

Zhang H, Shan B (2008) Historical records of heavy metal accumulation in sediments and the relationship with agricultural intensification in the Yangtze-Huaihe region, China. Sci Total Environ 399:113–120

Zhang W, Feng H, Chang J, Qu J, Xie H, Yu L (2009) Heavy metal contamination in surface sediments of Yangtze River intertidal zone: an assessment from different indexes. Environ Pollut 157:1533–1543