Environ Sci Pollut Res (2016) 23:8940–8950
DOI 10.1007/s11356-016-6151-1

RESEARCH ARTICLE

Heavy metals in the surface sediments of the northern portion of the South China Sea shelf: distribution, contamination, and sources

Fangjian Xu[1] · **Xu Tian**[1] · **Feng Yin**[2] · **Yongfang Zhao**[3] · **Xuebo Yin**[3]

Received: 20 August 2015 / Accepted: 20 January 2016 / Published online: 29 January 2016

Abstract The concentrations of seven heavy metals (Cr, Ni, Cu, Zn, As, Cd, and Pb) in the surface sediments of the northern portion of the South China Sea (SCS) shelf collected between 2012 and 2014 were measured to assess the potential contamination levels and determine the environmental risks that are associated with heavy metals in the area. The measured concentrations in the sediments were 12.4–72.5 mg kg^{-1} for Cr, 4.4–29.2 mg kg^{-1} for Ni, 7.1–38.1 mg kg^{-1} for Cu, 19.3–92.5 mg kg^{-1} for Zn, 1.3–12.1 mg kg^{-1} for As, 0.03–0.24 mg kg^{-1} for Cd, and 8.5–24.4 mg kg^{-1} for Pb. These results indicate that the heavy metal concentrations in the sediments generally meet the China Marine Sediment Quality criteria and suggest that the overall sediment quality of the northern portion of the SCS shelf has not been significantly impacted by heavy metal pollution. However, the enrichment factor (EF) and geoaccumulation index (I_{geo}) clearly show that elevated concentrations of Cd occur in the region. A Pearson's correlation analysis was performed, and the results suggest that Cr, Ni, Cu, and Zn have a natural origin; Cd is primarily sourced from anthropogenic activities, with partial lithogenic components, and As and Pb may be affected by factors such as varying input sources or pathways (i.e., coal burning activities and aerosol precipitation). Heavy metal contamination mostly occurred to the east of Hainan Island, mainly because of the rapid economic and social developments in the Hainan Island. The results of this study will be useful for marine environment managers for the remediation of pollution sources.

Keywords Heavy metals · Sediment contamination · Geoaccumulation index · Continental shelf · South China Sea · Hainan Island

Introduction

Urban and industrial activities discharge significant amounts of pollutants (including heavy metals) into the marine environment, and these pollutants directly affect the coastal systems where they are often deposited. In recent decades, rapid industrialization and economic development in China, especially in coastal areas, have resulted in severe environmental pollution (Zheng et al. 2008; Zhang et al. 2009; Qiu and Yu 2011; Xia et al. 2011a, b; Pan and Wang 2012; Fu et al. 2013; Hu et al. 2013a; Li et al. 2013; Xu et al. 2015; Zhou et al. 2015). As a natural sink of environmental pollutants, marine sediments are vulnerable and sensitive to environmental pollution, and they can be used as an indicator of potential environmental contamination (Zhang et al. 2009; Qiu and Yu 2011; Xia et al. 2011a, b; Balzer et al. 2013; Fu et al. 2013; Hu et al. 2013a; Li et al. 2013; da Silva et al. 2015; Xu et al. 2015; Zhou et al. 2015).

The South China Sea (SCS) is the largest tropical marginal sea, and the northern portion of the SCS shelf is among the largest sub-tropical shelves in the world. The open SCS has been intensively studied over the past several decades (Wei et al. 2006; Liu et al. 2010; Tian et al. 2010; Wan et al. 2015) and has been the focus of several national and international studies, such as the Tropical Ocean/Global Atmosphere (TOGA) program, the South China Sea Monsoon

Responsible editor: Philippe Garrigues

✉ Fangjian Xu
xufangjiangg@163.com

[1] School of Geosciences, China University of Petroleum, Changjiang West Road 66#, Qingdao, Shandong 266580, China

[2] Exploration Company, SINOPEC, Chengdu 610041, China

[3] Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China

Experiment (SCSMEX), and the Southeast Asian Time-series Study (SEATS) (Wong et al. 2007; Pan et al. 2015). However, the shelf seas around the rim of the SCS have received much less attention. Previous studies on the northern portion of the SCS shelf have focused on sub-regional phenomena, such as the influence of the Pearl River Estuary (Xia et al. 2004; Wei and Wu 2011; Yang et al. 2011), Pearl River outflow along the coast (Liu et al. 2009; Liu et al. 2014b), and upwelling off the Taiwan Bank (Lan et al. 2009) and Hainan Island (Jing et al. 2009). However, the quality of the sediments on the continental shelf has been rarely studied.

Over the previous decades, various indices have been developed to assess the heavy metal contamination of sediments and its ecological risk. These indices, such as the enrichment factor (EF) and geoaccumulation index (I_{geo}), estimate the impact of human activities on sediment quality and the sediment quality guidelines (SQGs), which are used to evaluate the ecological risk that is posed by heavy metals in sediments (Müller 1979; Müller 1981; Idris 2008; Hu et al. 2013a; Zhao et al. 2015). Furthermore, appropriate statistical approaches have increasingly been applied for environmental studies (Idris 2008; Hu et al. 2013a; Zhao et al. 2015). This study addresses the identified research gaps that would provide valuable information regarding the spatial distribution of the selected heavy metals in the northern portion of the SCS shelf. The aims of this paper are to (1) determine the concentrations of heavy metals (Cr, Ni, Cu, Zn, As, Cd, and Pb) in the surface sediments of the northern portion of the SCS shelf, (2) evaluate the potential for adverse biological impacts by comparing our results to the SQGs, (3) assess the heavy metal contamination by using the EF and I_{geo}, and (4) identify the heavy metal sources by using a Pearson's correlation analysis.

Regional setting

The northern portion of the SCS shelf is considered a passive continental margin (Yim et al. 2006) that stretches southwestward from a ridge system at approximately 23° N and 119° E, which delineates the southern end of the Taiwan Strait from the northeastern coasts of the Leizhou Peninsula and Hainan Island at approximately 20° N and 111° E. In addition, the northern portion of the SCS shelf extends from the southeastern coast of China to the shelf break near the 120-m isobath, which can be subdivided into three primary hydrographic subregimes, namely, the inner, middle, and outer shelf, which have water depths of <40 m, 40–90 m, and 90–120 m, respectively (Pan et al. 2015; Wong et al. 2015). The hydrographic characteristics of the inner shelf are heavily influenced by the input of terrestrial material, which results in lower salinity and higher suspended particle concentrations (Pan et al. 2015), whereas the hydrographic characteristics of the outer shelf are governed by mixing with the open oligotrophic SCS, which results in higher salinity and temperatures and lower suspended particle concentrations (Pan et al. 2015). The middle shelf contains a mixture of water from the inner and outer shelves. Superimposed on these shelf-wide patterns are secondary features that result from sub-regional processes, such as coastal upwelling (Jing et al. 2009; Su and Pohlmann 2009) and internal wave activities (Guo et al. 2012; Pan et al. 2015).

The highly urbanized Pearl River empties into the middle section of the northern portion of the SCS shelf with an annual sediment discharge of ~54–80 × 10^6 t (Zhang et al. 2008; Zhang et al. 2012). The total sediment discharge from local rivers in eastern Hainan Island is ~1 × 10^6 t year^{-1} (Liu et al. 2014a). Modern siliciclastic sediments that primarily originate as mud from the Pearl River are dominant from the coast to a depth of approximately 50 m on the middle shelf (Niino and Emery 1961; Yim et al. 2006; Liu et al. 2014b). Relic sediments have been identified at greater water depths (Niino and Emery 1961; Yim et al. 2006).

Monsoonal winds dominate over the northern portion of the SCS shelf, and they have a northeasterly direction in winter and a southwesterly direction in summer. The seasonal influence of monsoonal winds on the ocean circulation of the northern portion of the SCS shelf is clear, and wind-forced upper layer

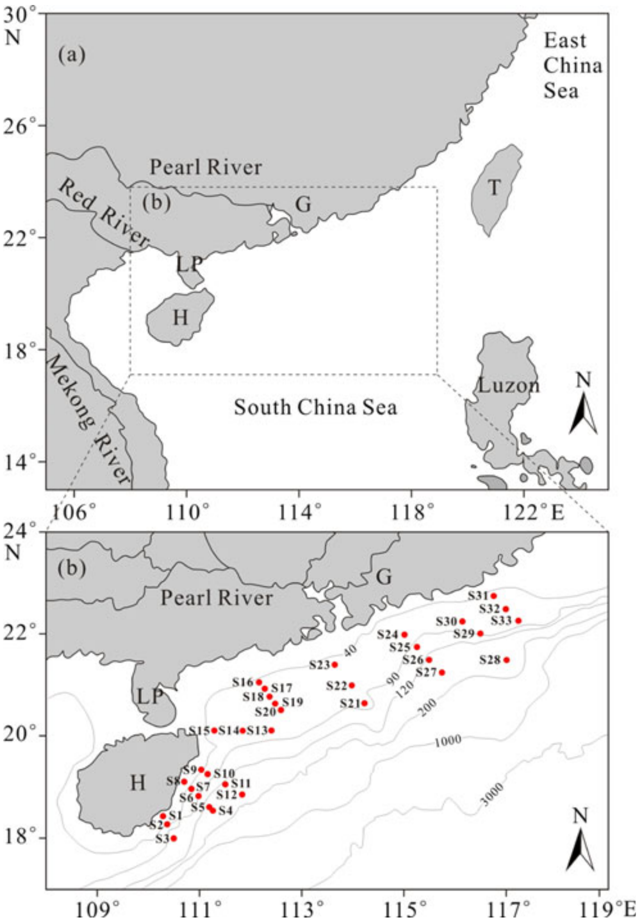

Fig. 1 Study area and locations of sampling sites in the northern portion of the SCS shelf. *T* Taiwan, *G* Guangdong, *LP* Leizhou Peninsula, and *H* Hainan Island

Table 1 Results from an analysis of certified reference materials. The concentrations are in mg kg^{-1}

Element	GBW07315		GBW07316		BCR-2		BHVO-2	
	Measured values	Certified values	Measured values	Certified values	Measured values	Certified values	Measured values	Certified values
Cr	60.5	59 ± 6	40.1	38 ± 2	17.3	18 ± 2	na	na
Ni	149	167 ± 12	115	108 ± 9	15.3	na	116	119 ± 7
Cu	319	357 ± 20	246	231 ± 10	24.9	19 ± 2	140	127 ± 7
Zn	146	137 ± 15	147	142 ± 22	140	127 ± 9	127	103 ± 6
As	7.65	7.1 ± 0.6	4.91	4.6 ± 0.5	0.774	na	1.12	na
Cd	0.316	0.250	0.284	0.3	2.02	na	0.230	na
Pb	36.1	37 ± 4	22.4	22 ± 5	11.8	11 ± 2	1.85	na

na not available

currents primarily flow along the shelf and move northeastward in summer and southwestward in winter (Fang et al. 2015). Coastal upwelling resulting from wind and/or topographic forcing has been reported in the northern portion of the SCS shelf during the summer off the Taiwan Bank (Lan et al. 2009) and the eastern coast of Hainan Island (Jing et al. 2009). Typhoons or tropical storms regularly affect the northern portion of the SCS shelf during the hot and wet summer monsoon season (Liu et al. 2011; Sun et al. 2011). The northern portion of the SCS shelf is dominated by irregular diurnal and mixed semi-diurnal microtides, mostly with <2 m tidal ranges (Krumme et al. 2012; Zhang et al. 2013). The maximum tidal current velocity is less than 0.5 m s^{-1} (Liu et al. 2002). The prevailing direction of both regular and strong waves is from the southeast. The average wave height is 1.06 m, and the maximum wave height is 4 m (Wang et al. 2013). Therefore, their effect on sediment erosion should be minor.

Materials and methods

Sampling

The sampling sites that were chosen for this study were located along the continental shelf south of Guangdong and east of Hainan Island at water depths from 30 to 130 m below the current sea level. A total of 33 surface sediment (0–5 cm) samples were collected by using a Van Veen grab sampler using a small vessel by R/V Shiyan 3 from the South China Sea Institute of Oceanology, Chinese Academy of Sciences between 2012 and 2014 (Fig. 1). All the samples were refrigerated at 4 °C until analysis.

Sedimentary properties

All the samples that were used for the grain-size analysis were pre-treated with excess 30 % H_2O_2 and 1 mol L^{-1} HCl in a water bath at 60 °C for 1 h to remove the organic matter and calcium carbonate, respectively. The suspension was centrifuged twice at 3500 rpm for 6 min with distilled water, and the supernatant was discarded each time. Subsequently, the samples were dispersed and homogenized by using ultrasound and then passed through a Mastersizer 3000 laser particle analyzer at the First Institute of Oceanography, State Oceanic Administration, China. This facility can measure grain sizes from 0.01 to 3500 μm with a measurement repeatability error of <1 %. The textures of the sediment samples were classified according to the Udden-Wentworth grade scale based on the relative percentages of clay (<4 μm), silt (4–63 μm), and sand (63–2000 μm) (Wentworth 1922).

Sediment geochemistry

The chemical analysis samples were also pre-treated with excess 30 % H_2O_2 and 1 mol L^{-1} HCl in a water bath at 60 °C for

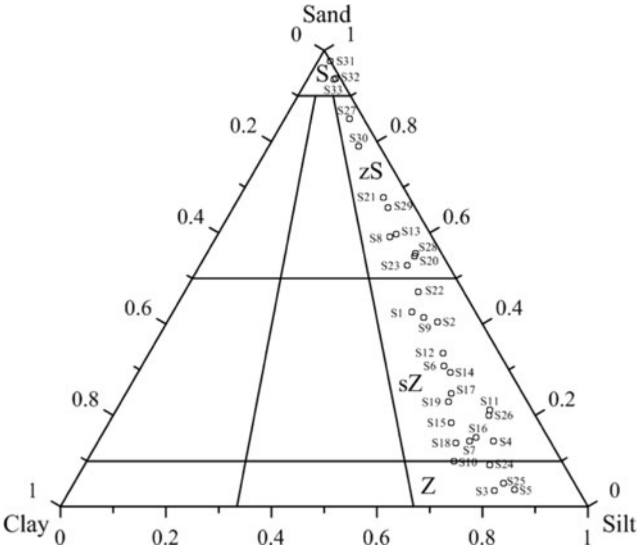

Fig. 2 Ternary classification diagram of the surface sediment samples based on Folk et al. (1970). *Z* silt, *sZ* sandy silt, *zS* silty sand, *S* sand

1 h to remove the organic matter and calcium carbonate, respectively. The suspension was centrifuged twice at 3500 rpm for 6 min with distilled water, and the supernatant was discarded. The residues of the samples were heated until dry at 60 °C and then ground into a powder by using an agate mortar and pestle. Approximately 0.04 g of powdered sample was then digested with an $HF + HNO_3 + HClO_4$ acid mixture in Teflon vessels. The major and heavy element concentrations were determined at the Institute of Oceanology, Chinese Academy of Sciences (IOCAS) by using a Thermo Icap6300 ICP-AES and a Perkin-Elmer ELAN DRC II ICP-MS, respectively. The analytical accuracy was assessed by comparison with selected certified reference materials from the United States Geological Survey (USGS) and China (BCR-2, BHVO-2, GBW07315, and GBW07316). Overall, the measured values of the reference material were within the range of the certified values (Table 1), indicating satisfactory recovery. Because the concentrations and spatial distribution of heavy metals may be related to the grain size, Pearson correlation coefficients were calculated for these parameters by using the statistical software SPSS (Version 19).

Results and discussion

Sediment types

The types of sediment were identified (Fig. 2) according to the ternary diagram of Folk's classification (Folk et al. 1970) and are listed in Table 2.

Table 2 Aluminum (%) and heavy metal concentrations (mg kg^{-1}) and other general characteristics of the sediments from the northern portion of the SCS shelf

Sampling site	Sediment type	Mz/φ	Al	Cr	Ni	Cu	Zn	As	Cd	Pb
S1	Sandy silt	5.0	11.8	54.2	24.0	29.8	82.9	6.2	0.18	18.6
S2	Sandy silt	4.9	10.3	53.3	23.2	30.3	81.4	9.1	0.17	22.6
S3	Silt	6.4	17.2	72.5	29.1	38.1	92.2	8.4	0.22	14.9
S4	Sandy silt	5.7	13.4	67.2	24.8	29.4	78.7	2.7	0.14	11.1
S5	Silt	6.1	13.2	69.5	28.4	32.1	91.6	4.0	0.18	12.5
S6	Sandy silt	5.2	13.1	62.7	25.6	31.3	85.2	8.9	0.21	17.0
S7	Sandy silt	5.9	14.7	64.3	27.0	35.5	87.1	9.4	0.24	17.9
S8	Silty sand	4.3	13.1	61.7	26.0	33.4	86.5	9.0	0.16	22.4
S9	Sandy silt	4.8	9.0	40.0	18.8	22.4	63.8	4.4	0.12	18.4
S10	Sandy silt	6.4	11.2	52.1	22.3	27.1	73.5	6.4	0.22	15.9
S11	Sandy silt	5.3	10.9	58.1	27.7	25.5	80.9	2.9	0.17	17.2
S12	Sandy silt	5.1	9.8	61.6	28.7	23.7	83.1	12.1	0.15	13.0
S13	Silty sand	4.0	6.3	35.7	11.0	14.5	37.8	1.9	0.07	11.5
S14	Sandy silt	5.2	7.8	41.7	20.5	17.0	56.6	2.3	0.14	16.0
S15	Sandy silt	5.9	13.6	63.1	26.8	32.5	87.6	7.8	0.19	18.0
S16	Sandy silt	5.9	13.0	59.6	27.1	30.1	92.5	5.5	0.16	24.4
S17	Sandy silt	5.6	9.9	49.2	24.0	24.0	74.4	3.8	0.18	20.5
S18	Sandy silt	6.2	8.7	46.5	23.5	20.1	65.2	2.9	0.14	19.6
S19	Sandy silt	5.7	9.8	54.4	25.8	24.4	77.6	3.3	0.14	21.3
S20	Silty sand	3.6	6.4	34.4	17.6	13.9	44.2	1.3	0.10	13.9
S21	Silty sand	2.8	5.1	24.4	10.2	10.7	31.6	1.7	0.24	11.5
S22	Sandy silt	4.4	8.5	44.7	20.1	19.8	65.8	3.0	0.12	18.5
S23	Silty sand	4.1	6.3	29.3	12.3	14.4	40.1	2.7	0.08	17.4
S24	Silt	6.1	13.8	62.3	21.8	25.9	69.1	3.4	0.13	11.4
S25	Silt	6.2	12.8	65.2	21.6	25.9	65.5	2.0	0.15	8.5
S26	Sandy silt	5.4	11.6	57.8	19.4	23.1	58.6	1.7	0.12	10.2
S27	Silty sand	2.9	4.9	25.1	9.1	10.2	33.4	6.8	0.06	13.0
S28	Silty sand	4.2	9.2	46.0	15.3	21.1	51.6	1.9	0.09	11.1
S29	Silty sand	4.0	8.8	45.0	13.2	16.5	43.7	1.5	0.10	10.7
S30	Silty sand	3.4	8.2	41.4	12.0	16.0	38.7	3.4	0.15	12.7
S31	Sand	1.9	5.3	12.4	4.4	7.1	19.3	1.4	0.03	14.5
S32	Sand	2.5	5.7	25.8	7.1	10.1	27.0	2.1	0.06	11.6
S33	Sand	2.8	6.8	27.5	9.4	12.2	32.2	2.5	0.06	10.5

Four samples (S3, S5, S24, and S25) were classified as silt, with sand, silt, and clay contents of 5.4, 80.7, and 13.9 %, respectively. Nine samples (S8, S13, S20, S21, S23, S27, S28, S29, and S30) were classified as silty sand, with sand, silt, and clay contents of 64.3, 30.2, and 5.5 %, respectively. Three samples (S31, S32, and S33) were classified as sand, with sand, silt, and clay contents of 95.0, 4.3, and 0.7 %, respectively. The remaining samples were classified as sandy silt, with sand, silt, and clay contents of 25.9, 61.6, and 12.5 %, respectively. The mean grain size (Mz) of the sediments varied from 1.93 to 6.37 φ and averaged 4.78 ± 1.25 φ.

Sediment geochemistry

As shown in Table 2, the concentrations of the metals in the surface sediments from the study area were 4.9–17.2 % for Al, 12.4–72.5 mg kg^{-1} for Cr, 4.4–29.2 mg kg^{-1} for Ni, 7.1–38.1 mg kg^{-1} for Cu, 19.3–92.5 mg kg^{-1} for Zn, 1.3–12.1 mg kg^{-1} for As, 0.03–0.24 mg kg^{-1} for Cd, and 8.5–24.4 mg kg^{-1} for Pb. The mean values of the heavy metal concentrations in the northern portion of the SCS shelf were comparable to or lower than those in other regions, such as Liaodong Bay (Hu et al. 2013c), Bohai Bay (Gao and Chen 2012), the Yangtze River Estuary (Wang et al. 2015), and the Pearl River Estuary (Yu et al. 2010) in China, as listed in Table 3. In addition, the metal concentrations in the northern portion of the SCS shelf were significantly lower than those in other larger industrialized/urban ports and estuaries around the world, such as Masan Bay in Korea (Hyun et al. 2007), the Gironde Estuary in France (Larrose et al. 2010), and the Guadiana Estuary in Spain (Delgado et al. 2010).

Assessment of potential ecological risk

Marine Sediment Quality Standards (GB 18668–2002) were promulgated by the China State Bureau of Quality and Technical Supervision (CSBTS 2002, Table 3) to prevent and control marine sediment pollution, protect marine life and resources, encourage the sustainable use of marine resources, maintain marine ecological equilibrium, and protect human health. GB 18668–2002 contains three criteria for marine sediments: the primary criteria (MSQ–1) for metal toxicity to wildlife and humans; the secondary criteria (MSQ–2) for general industries and coastal tourism; and the tertiary criteria (MSQ–3) for harbors and ocean exploration. According to the Marine Sediment Quality Standards (GB 18668–2002), the average concentrations of most of the heavy metals in the northern portion of the SCS shelf's surface sediments were below or close to the primary standard criteria. Among the 33 sampling sites, only two sites exceeded the primary criteria for Cu, whereas they met the secondary standard criteria. Because Ni standards were not available in the GB 18668–2002, we could not evaluate the sediment quality with respect

Table 3 Mean values and ranges of heavy metals in the surface sediments from the northern portion of the SCS shelf. Metal concentrations from other coastal areas, the upper continental crust (UCC), and the Marine Sediment Quality standard criteria are also listed (unit, mg kg^{-1})

Locations	Northern SCS shelf		Pearl River Estuary, China	Yangtze River Estuary, China	Coastal Bohai Bay, China	Liaodong Bay, China	Masan Bay, Korea	Guadiana Estuary, Spain	Gironde Estuary, France	UCC	MSQ–1[a]	MSQ–2[a]
	Range	Mean	Mean	Mean	Mean	Mean	Mean	Mean	Mean	Mean		
Cr	12.4–72.5	48.8 ± 15.4	106 ± 11.4	79.1	101	46.4	67.07	19.2 ± 0.46	78.4	92	80	150
Ni	4.4–29.2	19.9 ± 7.2	36.7 ± 6.0	31.9	40.7	22.5	28.84	27.8 ± 0.75	31.7	47	na	na
Cu	7.1–38.1	22.7 ± 8.3	45.7 ± 15.4	24.7	38.5	19.4	43.40	50.0 ± 1.76	24.5	28	35	100
Zn	19.3–92.5	63.6 ± 22.1	176.8 ± 43.4	82.9	131.1	71.7	206.26	168 ± 7.10	168	67	150	350
As	1.3–12.1	4.4 ± 2.9	na	9.1	na	8.3	na	25.5 ± 1.21	18.7	4.8	20	65
Cd	0.03–0.24	0.14 ± 0.05	na	0.19	0.22	na	1.24	0.20 ± 0.02	0.48	0.09	0.5	1.5
Pb	8.5–24.4	15.4 ± 4.2	57.9 ± 11.9	23.8	34.7	31.8	43.97	32.9 ± 1.17	46.8	17	60	130
References	This study		Yu et al. 2010	Wang et al. 2015	Gao and Chen 2012	Hu et al. 2013c	Hyun et al. 2007	Delgado et al. 2010	Larrose et al. 2010	Rudnick and Gao 2003	CSBTS 2002	CSBTS 2002

na not available

[a] MSQ–1 and MSQ–2 are the Marine Sediment Quality standard criteria (GB 18668–2002), which were issued by the China State Bureau of Quality and Technical Supervision (CSBTS)

to Ni. In general, the concentrations of the seven heavy metals in this study suggest that the overall sediment quality in the study area has not been significantly impacted by heavy metal pollution.

Threshold effect level (TEL)/probable effect level (PEL) SQGs were also applied to assess the degree to which the sediment-associated metals might adversely affect aquatic organisms, and these SQGs were designed to assist in the interpretation of sediment quality (Long et al. 1995; MacDonald et al. 2000). The TELs are intended to represent chemical concentrations below which adverse biological effects rarely occur, and the PELs are intended to represent chemical concentrations above which adverse biological effects frequently occur (Long et al. 1995; MacDonald et al. 2000). A comparison of the TEL and PEL SQGs indicates that the concentrations of Cr, Ni, Cu, Zn, As, Cd, and Pb were below the TEL for 52, 30, 33, 100, 79, 100, and 100 % of the sample sites, respectively. The remaining samples all fell in the range between the TEL and PEL (Table 4). Therefore, the Cr, Ni, Cu, and As in the northern portion of the SCS shelf are likely to cause occasional adverse biological effects on the local aquatic ecosystems.

Anthropogenic enrichment of heavy metals

To better understand the current environmental status and assess the metal contamination in the northern portion of the SCS shelf, both the EF and I_{geo} were utilized to differentiate the metal sources (anthropogenic source vs. natural origin) and evaluate the degree of anthropogenic impacts. In this study, the EF were calculated by using the following equation: $EF = (X_{sample}/Al_{sample})/(X_{baseline}/Al_{baseline})$, where X_{sample}, $X_{baseline}$, Al_{sample}, and $Al_{baseline}$ represent the heavy metal concentrations and aluminum contents of the samples and background references, respectively. The elemental abundance in the upper continental crust (UCC, Table 3, Rudnick and Gao 2003) was used as the reference baseline because of a lack of data on the background concentrations in the study area. In general, EF values of 0.5–1.5 are typical of heavy metal levels and reflect regional rock compositions, whereas EF values >1.5 indicate non-crustal contributions and/or non-natural weathering processes (e.g., anthropogenic influences) (Zhang and Liu 2002).

The EF of the surface sediments in the study area are shown in Fig. 3, and they are in the order Cd > Pb > Zn > As > Cu > Cr > Ni. The average EF of Cu (1.2 ± 0.2), Cr (0.8 ± 0.1), and Ni (0.6 ± 0.2) were less than 1.5 in the northern portion of the SCS shelf, which suggests that these metals are not a major concern, although several sites showed minor enrichment in these metals. However, moderate enrichment in Pb, Zn, and As was also found in certain areas, with 18 sites enriched in Pb (1.6 to 2.5, mean of 2.0), 16 sites enriched in Zn (1.5 to 2.0, mean of 1.7), and 11 sites enriched in As (1.6 to 4.5, mean of 2.4). These EF values that exceed 1.5 indicate minor to moderate Pb, Zn, and As contamination in the study area and suggest that the metals may originate from both natural and anthropogenic sources. In contrast, the average EF of Cd (2.5 ± 1.2) was greater than 1.5, which suggests that Cd contamination occurs in the northern portion of the SCS shelf.

Similar to EF, the I_{geo} can also be used to estimate the degree of metal pollution. The I_{geo} values were calculated with the following equation: $I_{geo} = \log_2(C_n/1.5B_n)$, where C_n is the concentration of a metal and B_n is the geochemical background concentration of that metal. The factor of 1.5 represents a background matrix correction factor that includes possible variations in the background values because of lithogenic effects (Müller 1979). The elemental abundance of the UCC (Rudnick and Gao 2003) was also adopted as the geochemical background concentration for the metals. The calculated I_{geo} values in the northern portion of the SCS shelf sediments were −3.47 to −0.93 for Cr, −4.01 to −1.27 for Ni, −2.56 to −0.14 for Cu, −2.38 to −0.12 for Zn, −2.51 to 0.75 for As, −2.14 to 0.85 for Cd, and −1.58 to −0.06 for Pb. Based on the Müller scale (Müller 1981), the average I_{geo} values below zero that were observed for Cr (−1.59 ± 0.57), Ni (−1.95 ± 0.66), Cu (−1.00 ± 0.61), Zn (−0.77 ± 0.60), and Pb (−0.78 ± 0.39) suggest a lack of pollution by these metals in the region. However, the I_{geo} values for Cd (−0.07 ± 0.68) suggest moderate Cd pollution in this area. Although the I_{geo}

Table 4 Comparison between the heavy metal concentrations (mg kg^{-1}) in the northern portion of the SCS shelf and sediment quality guidelines (SQGs), with the percentage of samples in each guideline

Sediment quality guidelines	Metal concentration (mg kg^{-1})						
	Cr	Ni	Cu	Zn	As	Cd	Pb
TEL	52.3	15.9	18.7	124	7.2	0.68	30.2
PEL	160.4	42.8	108.2	271	41.6	4.2	112.2
Compared with TEL and PEL (% of sample in each guideline)							
<TEL (%)	52	30	33	100	79	100	100
≥TEL < PEL (%)	48	70	67	0	21	0	0
≥PEL (%)	0	0	0	0	0	0	0

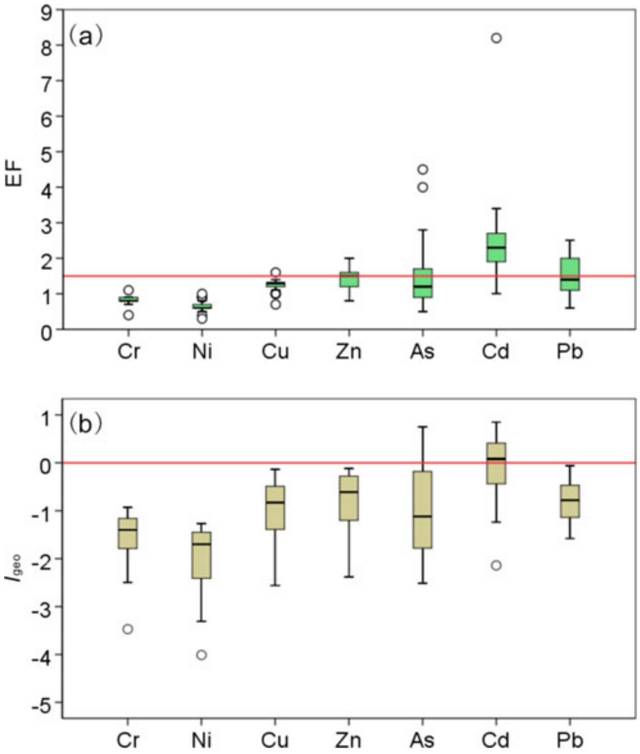

Fig. 3 Box-and-whisker plots for the **a** EF and **b** I_{geo} of heavy metals (Cr, Ni, Cu, Zn, As, Cd, and Pb) in the surface sediments from the northern portion of the SCS shelf. Both the EF and I_{geo} suggest moderate Cd pollution in the study area

values for As (−1.00 ± 0.94) were less than zero, several sites had positive values, indicating minor to moderate metal pollution.

Several sites had positive I_{geo} values for Cd and As, demonstrating minor to moderate metal pollution. Most of these sites occurred to the east of Hainan Island (Fig. 4a, b), where the sediments are mostly sandy silt and silt (Fig. 4c). This result suggests that the sediment granulometry can affect heavy metal concentrations in marine environments (Cai et al. 2011; Hu et al. 2013b).

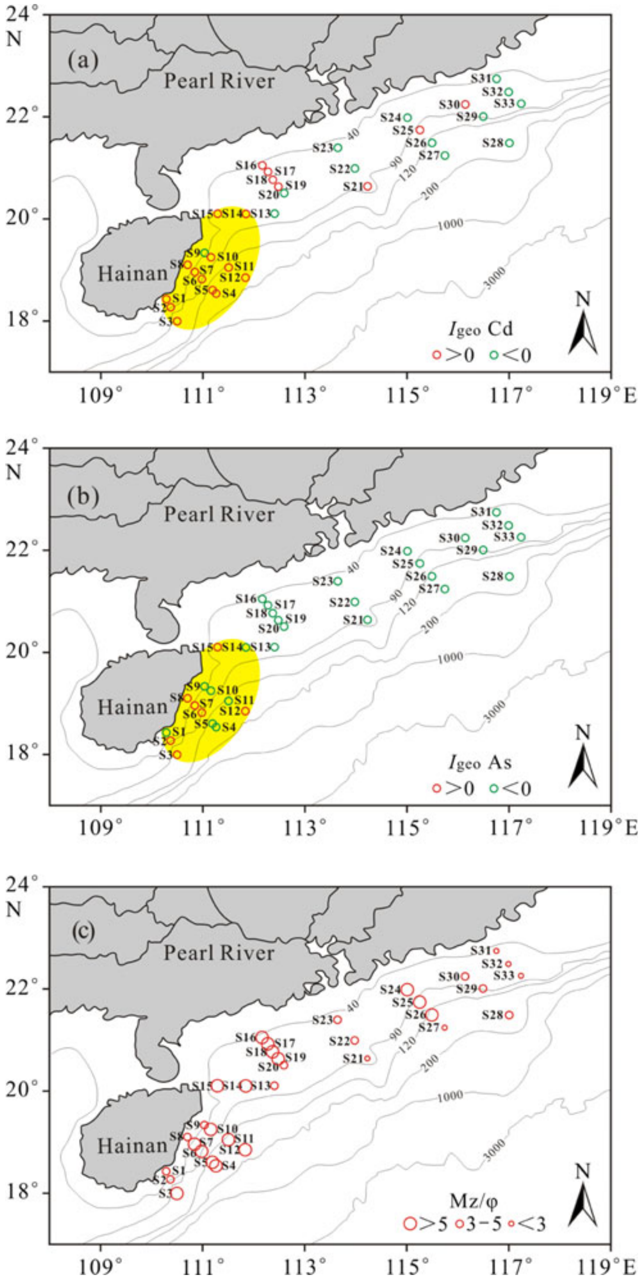

Fig. 4 Spatial distribution of the I_{geo} values for **a** Cd and **b** As, and **c** the mean grain size (Mz) of the surface sediments in the northern portion of the SCS shelf. The *yellow shaded area* indicates the heavy Cd and As contamination in the study area

Pearson's correlation coefficients were calculated to explore the relationship among the major element (Al), heavy metals (Cr, Ni, Cu, Zn, As, Cd, and Pb), and Mz in the surface sediments (Table 5). Strong positive correlations were observed among Cr, Ni, Cu, and Zn and between these metals and Al and Mz. Al is a structural element of terrigenous aluminosilicates and a primary lithogenic component, and the correlations between Al and Cr, Ni, Cu, and Zn suggest that these metals are likely associated with fine-grained terrigenous sediments because of their greater specific surface area (Williams et al. 1994; Hu et al. 2013b). Thus, Cr, Ni, Cu, and Zn most likely have a natural source that is related to the erosion of parent rocks and weathering crusts. Cd presented moderate positive correlations with other metals and Mz; however, the EF and I_{geo} results suggest that Cd is influenced by anthropogenic inputs. Previous studies have shown that the Cd distributions were closely related to the intensive usage of phosphate fertilizers (Jones and Johnston 1989; Zhang and Shan 2008; Xia et al. 2011a, b). The continuous application of these fertilizers and other soil amendments potentially exacerbates the accumulation of heavy metals in agricultural soils (Huang et al. 2007; Lambert et al. 2007). In addition, Cd might originate from the alloying, electroplating, and dyeing industries (Li et al. 2009; Xu et al. 2015). More recently, Zhao et al. (2015) found that the Cd in the surface sediments of rivers from eastern Hainan Island was predominantly sourced

Table 5 Pearson's correlation matrix for heavy metals (Cr, Ni, Cu, Zn, As, Cd, and Pb), Al, and mean grain-size (Mz)

	Mz	Al	Cr	Ni	Cu	Zn	As	Cd
Al	0.816**							
Cr	0.871**	0.942**						
Ni	0.876**	0.832**	0.910**					
Cu	0.819**	0.952**	0.932**	0.902**				
Zn	0.849**	0.872**	0.913**	0.977**	0.953**			
As	0.342	0.506**	0.500**	0.572**	0.633**	0.639**		
Cd	0.616**	0.645**	0.637**	0.698**	0.722**	0.707**	0.535**	
Pb	0.296	0.215	0.194	0.477**	0.412*	0.525**	0.439*	0.347*

**Correlation is significant at the 0.01 level (two-tailed)

*Correlation is significant at the 0.05 level (two-tailed)

from anthropogenic sources. Therefore, Cd is primarily sourced from anthropogenic activities and partially from lithogenic components.

Significant correlations were not observed between As and Pb and other metals or between As or Pb and Mz, which suggest that the distribution of As and Pb in the sediments of the northern portion of the SCS shelf could be affected by factors such as varying input sources or pathways (e.g., coal burning activities and aerosol precipitation) (Li et al. 2000; Gao and Chen 2012; Hu et al. 2013b). Similar situations were also found in the Pearl River Estuary (Li et al. 2000) and the Changhua River Estuary of western Hainan Island (Hu et al. 2013b).

As discussed above, the average concentrations of most of the heavy metals in the northern portion of the SCS shelf surface sediments were below or close to the China Marine Sediment Quality Standards (MSQ–1). However, a comparison of the TEL and PEL SQGs indicates that several heavy metals in the study area are likely to cause occasional adverse biological effects on the local aquatic ecosystems. As mentioned above, EF values that are higher than 1.5 and positive I_{geo} values are indicators of anthropogenic sources and heavy metal pollution. In this study, the EF and I_{geo} values of Cd (2.5 ± 1.2 and −0.07 ± 0.68, respectively) clearly show that elevated concentrations of Cd occur in the region. Therefore, both EF and I_{geo} are more suitable tools for the assessment of heavy metal pollution.

As shown in Fig. 4, the most apparent feature of the metal distribution is that the contamination in eastern Hainan Island was generally higher than that in the other areas. Over the last 50–60 years, Hainan's coastal zone and its hinterland underwent considerable changes because of continuously increasing human activities; this phenomenon has been especially characteristic since the 1980s, when China initiated its economic innovation and later established Hainan Province in 1988 (Zhang et al. 2013). The population of Hainan Island was 2.59 million in 1952. By 2013, the population had increased to 8.95 million. The gross domestic product (GDP) of Hainan increased from 1.64 billion Yuan RMB in 1987 to 314.65 billion Yuan RMB in 2013, i.e., more than 190 times greater. The cultivated land of Hainan Island was 344.7×10^3 ha during the early 1950s and increased to approximately 418.2×10^3 ha by 2013. The surface area for marine aquaculture increased from 0.2×10^3 ha in 1957 to 14.5×10^3 ha in 2010 (Zhang et al. 2013). The amount of chemical fertilizers and pesticides that have been applied has also increased. For example, the application of chemical fertilizers in 2013 amounted to 124.05×10^4 t year^{-1}, the overall consumption of pesticides was 4.35×10^4 t year^{-1}, and the total waste water discharge was $36{,}214.7 \times 10^4$ t year^{-1} (Hainan Municipal Statistics Bureau 2014). Therefore, large amounts of heavy metals (especially Cd and As) from industries, sewage wastewater, and marine aquaculture were discharged directly into the eastern Hainan Island continental shelf because of the rapid economic and social developments in this region and caused the deterioration of the local aquatic environment.

Conclusions

The concentration and spatial distribution of heavy metals (Cr, Ni, Cu, Zn, As, Cd, and Pb) and sediment grain sizes were analyzed for the surface sediments of the northern portion of the SCS shelf. The heavy metal concentrations in these sediments generally met the criteria of the China Marine Sediment Quality Standards (GB18668–2002). Based on the effect-range classification with TEL and PEL SQGs, however, the concentrations of Cr, Ni, Cu, and As are likely to occasionally cause adverse biological effects on the local aquatic ecosystems. Pearson's correlation analysis indicated that fine-grained particles are an important carrier of heavy metals. Cr, Ni, Cu, and Zn are predominantly sourced from lithogenic components in the surrounding area, while Cd is primarily sourced from anthropogenic activities (e.g., phosphate fertilizers that are used in nearby catchments) and partially from lithogenic components. The As and Pb concentrations could be influenced by different sources or pathways (e.g., coal burning activities and aerosol precipitation). The EF and I_{geo} values clearly showed that Cd contamination (2.5 ± 1.2 and −0.07 ± 0.68, respectively) occurs in the study area. Heavy metal contamination (especially Cd and As) mostly occurs to the east of Hainan Island because of the rapid economic and social developments in the region. This work represents the current state of the sediment quality in the northern portion of the SCS shelf. Greater attention should be paid to anthropogenic sources of heavy metals, i.e., Hainan Island, because of further industrialization and economic development in the northern portion of the SCS shelf region.

Acknowledgments We especially thank Editor Philippe Garrigues and the anonymous reviewers for their constructive reviews on the early version of this paper. Many thanks to the crews on the South China Sea Open Cruise by R/V Shiyan 3, South China Sea Institute of Oceanology, Chinese Academy of Sciences. Funding for this research was provided by the National Natural Science Foundation of China (grant nos. 41430965 and 41106040), Qingdao Science and Technology Development Plan Projects (grant no. 13-1-4-197-jch), and Fundamental Research Fund for the Central Universities (grant nos. 14CX02038A and 12CX02003A).

References

Balzer W, Boehler E, Tang X, Ren J, Zhang J, Wang D (2013) Arsenic in solution, colloidal and particulate phases of East-Hainan estuaries. Cont Shelf Res 57:73–81. doi:10.1016/j.csr.2012.04.005

Cai MH, Lin J, Hong QQ, Wang Y, Cai MG (2011) Content and distribution of trace metals in surface sediments from the northern Bering Sea, Chukchi Sea and adjacent Arctic areas. Mar Pollut Bull 63(5-12):523–527. doi:10.1016/j.marpolbul.2011.02.007

CSBTS (2002) Marine sediment quality. Standards Press of China, Beijing **(in Chinese)**

da Silva YJAB, Cantalice JRB, Singh VP, do Nascimento CWA, Piscoya VC, Guerra SMS (2015) Trace element fluxes in sediments of an environmentally impacted river from a coastal zone of Brazil. Environ Sci Pollut Res 22(19):14755–14766. doi:10.1007/s11356-015-4670-9

Delgado J, Nieto JM, Boski T (2010) Analysis of the spatial variation of heavy metals in the Guadiana Estuary sediments (SW Iberian Peninsula) based on GIS-mapping techniques. Estuar Coast Shelf Sci 88(1):71–83. doi:10.1016/j.ecss.2010.03.011

Fang W, Guo P, Liu C, Fang G, Li S (2015) Observed sub-inertial current variability and volume transport over the continental shelf in the northern South China Sea. Estuar Coast Shelf Sci 157:19–31. doi:10.1016/j.ecss.2015.02.001

Folk RL, Andrews PB, Lewis DW (1970) Detrital sedimentary rock classification and nomenclature for use in New Zealand. New Zeal J Geol Geop 13(4):937–968. doi:10.1080/00288306.1970.10418211

Fu J, Tang X-L, Zhang J, Balzer W (2013) Estuarine modification of dissolved and particulate trace metals in major rivers of East-Hainan, China. Cont Shelf Res 57:59–72. doi:10.1016/j.csr.2012.06.015

Gao X, Chen C-TA (2012) Heavy metal pollution status in surface sediments of the coastal Bohai Bay. Water Res 46(6):1901–1911. doi:10.1016/j.watres.2012.01.007

Guo C, Vlasenko V, Alpers W, Stashchuk N, Chen X (2012) Evidence of short internal waves trailing strong internal solitary waves in the northern South China Sea from synthetic aperture radar observations. Remote Sens Environ 124:542–550. doi:10.1016/j.rse.2012.06.001

Hainan Municipal Statistics Bureau (2014) Hainan Statistical Yearbook. China Statistics Press, Beijing **(in Chinese)**

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(1-2):400–405. doi:10.1016/j.marpolbul.2013.08.020

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 20(6):4099–4110. doi:10.1007/s11356-012-1332-z

Hu B, Li J, Zhao J, Yang J, Bai F, Dou Y (2013c) Heavy metal in surface sediments of the Liaodong Bay, Bohai Sea: distribution, contamination, and sources. Environ Monit Assess 185(6):5071–5083. doi:10.1007/s10661-012-2926-0

Huang SS, Liao QL, Hua M, Wu XM, Bi KS, Yan CY, Chen B, Zhang XY (2007) Survey of heavy metal pollution and assessment of agricultural soil in Yangzhong district, Jiangsu Province, China. Chemosphere 67(11):2148–2155. doi:10.1016/j.chemosphere.2006.12.043

Hyun S, Lee C-H, Lee T, Choi J-W (2007) Anthropogenic contributions to heavy metal distributions in the surface sediments of Masan Bay, Korea. Mar Pollut Bull 54(7):1059–1068. doi:10.1016/j.marpolbul.2007.02.013

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(2):159–163. doi:10.1016/j.microc.2008.05.004

Jing ZY, Qi YQ, Hua ZL, Zhang H (2009) Numerical study on the summer upwelling system in the northern continental shelf of the South China Sea. Cont Shelf Res 29(2):467–478. doi:10.1016/j.csr.2008.11.008

Jones KC, Johnston AE (1989) Cadmium in cereal grain and herbage from long-term experimental plots at Rothamsted, UK. Environ Pollut 57(3):199–216. doi:10.1016/0269-7491(89)90012-2

Krumme U, Herbeck LS, Wang T (2012) Tide- and rainfall-induced variations of physical and chemical parameters in a mangrove-depleted estuary of East Hainan (South China Sea). Mar Environ Res 82:28–39. doi:10.1016/j.marenvres.2012.09.002

Lambert R, Grant C, Sauvé S (2007) Cadmium and zinc in soil solution extracts following the application of phosphate fertilizers. Sci Total Environ 378(3):293–305. doi:10.1016/j.scitotenv.2007.02.008

Lan K-W, Kawamura H, Lee M-A, Chang Y, Chan J-W, Liao C-H (2009) Summertime sea surface temperature fronts associated with upwelling around the Taiwan Bank. Cont Shelf Res 29(7):903–910. doi:10.1016/j.csr.2009.01.015

Larrose A, Coynel A, Schäfer J, Blanc G, Massé L, Maneux E (2010) Assessing the current state of the Gironde Estuary by mapping priority contaminant distribution and risk potential in surface sediment. Appl Geochem 25(12):1912–1923. doi:10.1016/j.apgeochem.2010.10.007

Li C, Kang S, Zhang Q (2009) Elemental composition of Tibetan Plateau top soils and its effect on evaluating atmospheric pollution transport. Environ Pollut 157(8-9):2261–2265. doi:10.1016/j.envpol.2009.03.035

Li R, Liu S, Zhang G, Ren J, Zhang J (2013) Biogeochemistry of nutrients in an estuary affected by human activities: the Wanquan River estuary, eastern Hainan Island, China. Cont Shelf Res 57:18–31. doi:10.1016/j.csr.2012.02.013

Li X, Wai OWH, Li YS, Coles BJ, Ramsey MH, Thornton I (2000) Heavy metal distribution in sediment profiles of the Pearl River estuary, South China. Appl Geochem 15(5):567–581. doi:10.1016/S0883-2927(99)00072-4

Liu J, Cai S, Wang S (2011) Observations of strong near-bottom current after the passage of Typhoon Pabuk in the South China Sea. J Marine Syst 87(1):102–108. doi:10.1016/j.jmarsys.2011.02.023

Liu JP, Xue Z, Ross K, Wang HJ, Yang ZS, Li AC, Gao S (2009) Fate of sediments delivered to the sea by Asian large rivers: long-distance transport and formation of remote alongshore clinothems. SEPM-Sediment Rec 7(4):4–9

Liu J, Clift PD, Yan W, Chen Z, Chen H, Xiang R, Wang D (2014a) Modern transport and deposition of settling particles in the northern South China Sea: sediment trap evidence adjacent to Xisha Trough. Deep Sea Res Pt I 93:145–155. doi:10.1016/j.dsr.2014.08.005

Liu Y, Gao S, Wang YP, Yang Y, Long J, Zhang Y, Wu X (2014b) Distal mud deposits associated with the Pearl River over the northwestern continental shelf of the South China Sea. Mar Geol 347:43–57. doi:10.1016/j.margeo.2013.10.012

Liu Z, Colin C, Li X, Zhao Y, Tuo S, Chen Z, Siringan FP, Liu JT, Huang C-Y, You C-F, Huang K-F (2010) Clay mineral distribution in surface sediments of the northeastern South China Sea and surrounding fluvial drainage basins: source and transport. Mar Geol 277(1-4):48–60. doi:10.1016/j.margeo.2010.08.010

Liu Z, Zhao H, Fan S, Chen S (2002) Geology of the South China Sea. Science Press, Beijing **(in Chinese)**

Long ER, Macdonald DD, Smith SL, Calder FD (1995) Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ Manage 19(1):81–97. doi:10.1007/BF02472006

Müller G (1979) Schwermetalle in den Sedimenten des Rheins-Veränderungen seit 1971. Umschau 79(24):778–783

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

MacDonald DD, Ingersoll CG, Berger TA (2000) Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Arch Environ Con Tox 39(1):20–31. doi:10.1007/s002440010075

Niino H, Emery KO (1961) Sediments of shallow portions of East China Sea and South China Sea. Geol Soc Am Bull 72(5):731–762. doi:10.1130/0016-7606(1961)72[731:SOSPOE]2.0.CO;2

Pan K, Wang W-X (2012) Trace metal contamination in estuarine and coastal environments in China. Sci Total Environ 421–422:3–16. doi:10.1016/j.scitotenv.2011.03.013

Pan X, Wong GTF, Tai J-H, Ho T-Y (2015) Climatology of physical hydrographic and biological characteristics of the Northern South China Sea Shelf-sea (NoSoCS) and adjacent waters: observations from satellite remote sensing. Deep Sea Res Part II 117:10–22. doi:10.1016/j.dsr2.2015.02.022

Qiu YW, Yu KF (2011) Accumulation of heavy metals in sediment of mangrove wetland from Hainan Island. J Trop Oceanogr 30(2):102–108 **(in Chinese with English abstract)**

Rudnick RL, Gao S (2003) Composition of the continental crust. In: Heinrich DH, Karl KT (eds) Treatise on geochemistry. Pergamon, Oxford, pp 1–64

Su J, Pohlmann T (2009) Wind and topography influence on an upwelling system at the eastern Hainan coast. J Geophys Res 114: doi:10.1029/2008JC005018

Sun Z, Hu J, Zheng Q, Li C (2011) Strong near-inertial oscillations in geostrophic shear in the northern South China Sea. J Oceanogr 67(4):377–384. doi:10.1007/s10872-011-0038-z

Tian J, Huang E, Pak DK (2010) East Asian winter monsoon variability over the last glacial cycle: insights from a latitudinal sea-surface temperature gradient across the South China Sea. Palaeogeogr Palaeoclimat Palaeoecol 292(1-2):319–324. doi:10.1016/j.palaeo.2010.04.005

Wan S, Toucanne S, Clift PD, Zhao D, Bayon G, Yu Z, Cai G, Yin X, Révillon S, Wang D, Li A, Li T (2015) Human impact overwhelms long-term climate control of weathering and erosion in southwest China. Geology 43(5):439–442. doi:10.1130/G36570.1

Wang D-r, Y-c L, J-x L (2013) Spatial differentiation of coral species related to wave energy along the Changqi coast, Hainan island, southern China. Cont Shelf Res 57:117–122. doi:10.1016/j.csr.2012.12.004

Wang H, Wang J, Liu R, Yu W, Shen Z (2015) Spatial variation, environmental risk and biological hazard assessment of heavy metals in surface sediments of the Yangtze River estuary. Mar Pollut Bull 93(1-2):250–258. doi:10.1016/j.marpolbul.2015.01.026

Wei G, Li X-H, Liu Y, Shao L, Liang X (2006) Geochemical record of chemical weathering and monsoon climate change since the early Miocene in the South China Sea. Paleoceanography 21:PA4214. doi:10.1029/2006PA001300

Wei X, Wu CY (2011) Holocene delta evolution and sequence stratigraphy of the Pearl River Delta in South China. Sci China Earth Sci 54(10):1523–1541. doi:10.1007/s11430-011-4238-6

Wentworth CK (1922) A scale of grade and class terms for clastic sediments. J Geol 30(5):377–392. doi:10.1086/622910

Williams TP, Bubb JM, Lester JN (1994) Metal accumulation within salt marsh environments: a review. Mar Pollut Bull 28(5):277–290. doi:10.1016/0025-326X(94)90152-X

Wong GTF, Ku T-L, Mulholland M, Tseng C-M, Wang D-P (2007) The SouthEast Asian Time-series Study (SEATS) and the biogeochemistry of the South China Sea—an overview. Deep Sea Res Part II 54(14-15):1434–1447. doi:10.1016/j.dsr2.2007.05.012

Wong GTF, Pan X, Li K-Y, Shiah F-K, Ho T-Y, Guo X (2015) Hydrography and nutrient dynamics in the Northern South China Sea Shelf-sea (NoSoCS). Deep Sea Res Part II 117:23–40. doi:10.1016/j.dsr2.2015.02.023

Xia N, Xue GC, Fu YR, Yang Y, Liu CZ, Ma RL (2011a) Analysis of ecological risk and the content situation of heavy metals in surface sediments of Hainan Island's inshore. Resour Environ Eng 25(3):244–247 **(in Chinese with English abstract)**

Xia P, Meng X, Yin P, Cao Z, Wang X (2011b) 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(1):92–99. doi:10.1016/j.envpol.2010.09.014

Xia XM, Li Y, Yang H, Wu CY, Sing TH, Pong HK (2004) Observations on the size and settling velocity distributions of suspended sediment in the Pearl River Estuary, China. Cont Shelf Res 24(16):1809–1826. doi:10.1016/j.csr.2004.06.009

Xu G, Liu J, Pei S, Gao M, Hu G, Kong X (2015) Sediment properties and trace metal pollution assessment in surface sediments of the Laizhou Bay, China. Environ Sci Pollut Res 22(15):11634–11647. doi:10.1007/s11356-015-4393-y

Yang S, Tang M, Yim WWS, Zong Y, Huang G, Switzer AD, Saito Y (2011) Burial of organic carbon in Holocene sediments of the Zhujiang (Pearl River) and Changjiang (Yangtze River) estuaries. Mar Chem 123(1-4):1–10. doi:10.1016/j.marchem.2010.07.001

Yim WWS, Huang G, Fontugne MR, Hale RE, Paterne M, Pirazzoli PA, Ridley Thomas WN (2006) Postglacial sea-level changes in the northern South China Sea continental shelf: Evidence for a post-8200 calendar yr BP meltwater pulse. Quatern Int 145–146:55–67. doi:10.1016/j.quaint.2005.07.005

Yu X, Yan Y, Wang W-X (2010) The distribution and speciation of trace metals in surface sediments from the Pearl River Estuary and the Daya Bay, Southern China. Mar Pollut Bull 60(8):1364–1371. doi:10.1016/j.marpolbul.2010.05.012

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(1-3):113–120. doi:10.1016/j.scitotenv.2008.03.036

Zhang J, Liu CL (2002) Riverine composition and estuarine geochemistry of particulate metals in China—weathering features, anthropogenic impact and chemical fluxes. Estuar Coast Shelf Sci 54(6):1051–1070. doi:10.1006/ecss.2001.0879

Zhang J, Wang DR, Jennerjahn T, Dsikowitzky L (2013) Land–sea interactions at the east coast of Hainan Island, South China Sea: a synthesis. Cont Shelf Res 57:132–142. doi:10.1016/j.csr.2013.01.004

Zhang S, Lu XX, Higgitt DL, Chen C-TA, Han J, Sun H (2008) Recent changes of water discharge and sediment load in the Zhujiang (Pearl River) Basin, China. Global Planet Change 60(3-4):365–380. doi:10.1016/j.gloplacha.2007.04.003

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(5):1533–1543. doi:10.1016/j.envpol.2009.01.007

Zhang W, Wei X, Zheng J, Zhu Y, Zhang Y (2012) Estimating suspended sediment loads in the Pearl River Delta region using sediment rating curves. Cont Shelf Res 48:35–46. doi:10.1016/j.csr.2012.02.017

Zhao D, Wan S, Yu Z, Huang J (2015) Distribution, enrichment and sources of heavy metals in surface sediments of Hainan Island rivers, China. Environ Earth Sci 74(6):5097–5110. doi:10.1007/s12665-015-4522-4

Zheng N, Wang Q, Liang Z, Zheng D (2008) Characterization of heavy metal concentrations in the sediments of three freshwater rivers in Huludao City, Northeast China. Environ Pollut 154(1):135–142. doi:10.1016/j.envpol.2008.01.001

Zhou X, Sun L, Liu Y, Jia N, Cheng W, Wang Y (2015) Detection and calibration of anthropogenic lead emission in coastal sediments of China during the past 250 years. Environ Sci Pollut Res 22(20):16164–16172. doi:10.1007/s11356-015-4702-5