

Environmental status of Daya Bay surface sediments inferred from a sequential extraction technique

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ABSTRACT

The chemical partitioning of 12 trace metals (Ba, Cd, Co, Cu, Mn, Mo, Ni, Pb, Sc, Sr, U, Zn) in 9 surface sediments from Daya Bay, northern South China Sea, was studied by a four-step sequential extraction technique to assess their environmental/pollution status. The studied metals take on different fraction composition patterns, and some of them show significant spatial variation especially for Cd. A majority of the studied metals can be considered immobile because of their high percentages in the residual fraction. It seems that the Daya Bay surface sediments have not yet been polluted by the studied heavy metals which are used as parameters to classify marine sediment quality, i.e., Cd, Cu, Ni, Pb and Zn. For all metals except for Pb, the extent of anthropogenic influences on their total concentrations in the Daya Bay surface sediments is generally imperceptible. The metals' potential risks to the environment were assessed, and the results showed that they have generally no risk or low risk except for Cd, Mn and Sr.

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1. Introduction

Many elements that occur in low concentration in the Earth's crust are now mined extensively for use. Large quantities of different kinds of elements are discharged into the environment as contaminants each year by human activities. Marine sediment serves as one of the major reservoirs for all kinds of contaminants, including metals. The properties of metals in soils and sediments depend on the physicochemical form in which they occur (Gleyzes et al., 2002). Metals associate with sediments through various ways, including adsorption, complexation, and so on (Tessier et al., 1979). Changes in environmental conditions, such as temperature, pH, redox potential and organic ligand concentrations, can cause metals to be released from solid to liquid phase and sometimes cause contamination of surrounding waters in aquatic systems (Sahuquillo et al., 2003). Therefore, it cannot provide sufficient information about mobility, bioavailability and toxicity of metals if their total contents are studied alone.

The ecotoxicity and mobility of metals in the environment depend strongly on their specific chemical forms or method of binding. Consequently, toxic effects and biogeochemical pathways can only be studied on the basis of the determination of these forms

(Quevauviller, 1998). The sequential extraction technique is widely used now to provide information about the strength of metal binding to particulates, the phase associations of metals in solid matrix, etc. Many sequential extraction procedures have been put forward, among which the BCR (Community Bureau of Reference, now superseded by the Standards, Measurement and Testing Programme of the European Community) procedure is one of the most widely used procedures, and has been applied to soils, terrestrial/marine sediments and standard reference materials by a large number of researchers (e.g. Mossop and Davidson, 2003; Hjorth, 2004; Yuan et al., 2004).

Daya Bay is a busy region greatly affected by human activities. Its surrounding area is in the important economic development district in Guangdong, China. Petrochemical, plastic, printing and other industries as well as harbors are present. Two nuclear power stations, the Daya Bay and Ling'ao, which came into operation in 1994 and 2002 respectively, are situated at its western coast. Fish, shrimp and shellfish aquaculture are well developed in Daya Bay, and cage-cultured fishery is widespread in its inner waters. The main objectives of this study are to assess the environmental/pollution status of 12 trace metals in the surface sediments covering the whole Daya Bay area, including Ba, Cd, Co, Cu, Mn, Mo, Ni, Pb, Sc, Sr, U and Zn, by determining their concentrations and chemical forms in which they occur using the BCR sequential extraction procedure, and provide a background estimation of

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baseline data of these metals for future surveys on the responses of Daya Bay environment to anthropogenic activities.

2. Materials and methods

2.1. Study area

Daya Bay is a subtropical drowned valley bay of northern South China Sea located in the eastern coast of Guangdong Province, southern China (Fig. 1). It is one of a series of large embayments along the southern coast of China and covers an area of $\sim 600 \text{ km}^2$, with a width of about 20 km and a north–south length of about 30 km. The water depth in Daya Bay ranges from 6 to 16 m and the western part is deeper than the eastern part (Xu, 1989; Han, 1995). Although there is no large river discharging into the bay, there are over ten seasonal streams running into it in short distances along its coast (Han, 1995). The tidal current in Daya Bay is dominated by an irregular semidiurnal tide with an average tidal day of about 24.7 h. The mean tidal range is 1.01 m with a maximum of $\sim 2.57 \text{ m}$. Surface water of Daya Bay has an average resident time of 3.2 days (Wang et al., 1996). The annual mean precipitation in Daya Bay is 1827 mm and dry and rainy seasons can be easily distinguished (Han, 1995). The mean sedimentation rate of the bay is 0.9 cm a^{-1} (Han, 1995). Since the 1980s, there has been rapid expansion of aquacultural, industrial and agricultural activities in the area, with simultaneous developments in the construction of harbors, transportation and tourism; such dramatic changes have adversely affected the water quality in the bay (Zhou et al., 2001). The population has nearly doubled from 1986 to 2002; total industrial output value of main towns along the Daya Bay coast increased 7.8 times between 1993 and 2001 (Wang et al., 2008).

2.2. Sampling

Sediment samples were collected from nine locations in Daya Bay using a box grab sampler in January 2006 (Fig. 1), and related details are given in Table 1. Undisturbed top 5 cm sediments were sampled and placed in acid-rinsed polypropylene bags using a plastic spatula. Only one sample was collected from each sampling station. The samples were stored at $\sim 4^\circ \text{C}$ in the dark until further analysis.

2.3. Analytical methods

In general, sediment samples are usually dried and ground before extraction (e.g. Tokalioglu et al., 2000; Gismera et al., 2004). Although

the dry samples are easier to treat than the wet ones, it has been reported that sample drying could alter the solid phase distribution of trace elements (Rapin et al., 1986; Hjorth, 2004). Furthermore, the elemental concentrations in aquatic sediments are highly dependent on the grain size (Horowitz and Elrick, 1988; Howari and Banat, 2001), a triturating treatment could potentially alter the extractability of elements (e.g. Gilliam and Richter, 1988). To reduce the errors, here we used wet and unground sediments for the sequential extraction procedure. The homogenized samples were sub-sampled and put into 50 ml polypropylene centrifuge tubes and weighed to obtain the wet weight corresponding to approximately 0.5 g dry weight based on water content measurements.

The BCR sequential extraction procedure modified by Rauret et al. (1999) was used to obtain the information about the non-residual speciation of metals. The fourth step that involves digestion of residue from the third step was introduced to obtain an indication of the content of these elements associated with the residual components of sediment matrix (Rauret et al., 1999). The mixture of concentrated HF, HNO₃ and HClO₄ (5:2:1; Li et al., 2000) was used to leach all remaining metals in the residues instead of the so-called pseudototal digestion with aqua regia. The total digestion of sediments was performed by the same method used in the fourth step. The total content of metals in the sediments was estimated by summing up the results of the four steps, and accounts for 85–107% of the values from the total digestion experiment, which is within the range of other reports (e.g. Martin et al., 1998; Li et al., 2001; Yuan et al., 2004).

The sequential extraction protocol used, along with the sediment fractions from which metals are released, is summarized in Table 2. For each sample, the wet weight corresponding to approximately 0.5 g dry weight based on water content measurements was used. 0.1 g residue (dry weight) from step III was used to measure Fraction 4. Between the extraction steps, solid/liquid separation was achieved by centrifuging at 4000 rpm for 20 min, the resulting supernatant being decanted into polyethylene bottles and stored at 4°C until analysis. Residues were then washed with 10 ml de-ionized water (Milli-Q), shaken for 15 min, and centrifuged for 20 min at 4000 rpm, the supernatant being discarded. The sequential extraction procedure was carried out with no interruption once started (Ajay and van Loon, 1989). Inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500), calibrated with external standard solutions, was applied for the determination of Ba, Cd, Co, Cu, Mn, Mo, Ni, Pb, Sc, Sr, U and Zn. Indium and rhenium internal standards were used to improve calibration and reproducibility. The concentrations of Al were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Perkin-Elmer Optima 3300

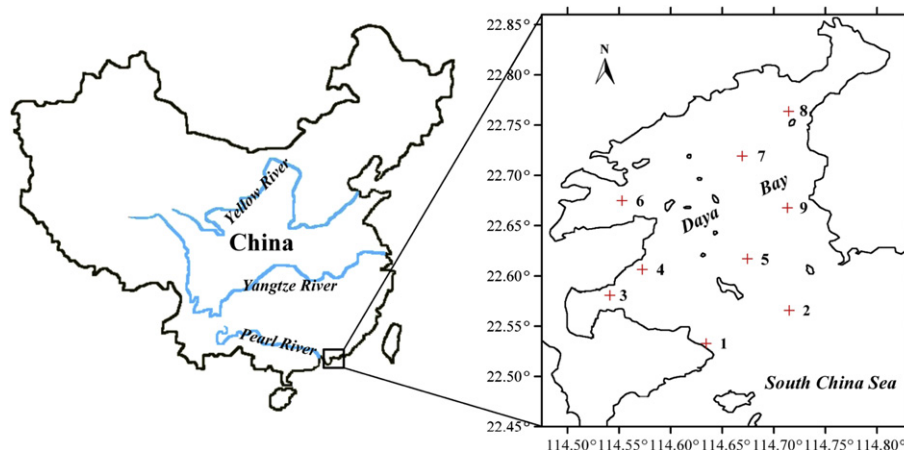


Fig. 1. Location of sampling stations in Daya Bay, northern South China Sea.

Table 1

The location, water depth and temperature of each sampling station and some bulk geochemical parameter values of the sediments sampled.

Station	Longitude (E)	Latitude (N)	Water depth (m)	Temperature (°C)	TOM (%)	CaCO ₃ (%)	Clay (%)	Silt (%)	Sand (%)
1	114°38.06'	22°31.97'	15.1	16.5	9.1	4.1	4.3	93.8	1.9
2	114°42.89'	22°33.95'	16.2	16.7	10.5	5.5	5.7	86.9	7.4
3	114°32.46'	22°34.85'	12.2	17.1	12.6	12.2	5.8	89.1	5.1
4	114°34.35'	22°36.39'	11.5	17.4	7.1	7.2	15.6	73.5	10.9
5	114°40.46'	22°37.03'	10.9	16.8	8.9	4.9	28.9	55.6	15.5
6	114°33.17'	22°40.49'	7.4	16.5	11.5	6.1	34.6	65.3	0.1
7	114°40.15'	22°43.16'	10.2	16.8	9.9	6.6	31.7	66.3	2.0
8	114°42.86'	22°45.82'	7.0	16.2	11.5	10.4	36.8	61.8	1.4
9	114°42.79'	22°40.06'	9.9	16.0	9.8	11.3	34.5	63.4	2.1

DV) to calculate the enrichment factor for each element. The Chinese national geostandard samples of GSS-1 and GSS-8 were used to control the analytical quality. The results were consistent with the reference values, and the differences were all within 10% (most were within 5%). All plastic and glassware were pre-cleaned by soaking in 10% HNO₃ (v/v) for at least 2 days, followed by soaking and rinsing with de-ionized water. All chemicals used in the experiment were analytical-reagent grade or better. Blank determinations were carried out for each set of analysis using the same reagents.

All data were corrected for dry weight of the sample. The water content of the sediment was determined gravimetrically by comparing the weight difference before and after heating an aliquot at 105 °C until constant weight. The percentage of water was used to convert substance content of the sediment from wet to dry weight base. The contents of total organic matter (TOM) and inorganic carbonate (CaCO₃) were estimated by loss-on-ignition (LOI) technique. After water content was measured, the sample was heated at 550 °C for 4 h to estimate TOM. Further heating at 1000 °C for 2 h was conducted to estimate CaCO₃ content (Rabenhorst, 1988). Both TOM and CaCO₃ were determined as a percentage of dry weight.

The sample granulometry was analyzed using a Malvern Mastersizer 2000 laser diffractometer capable of analyzing particle sizes between 0.02 and 2000 μm. The percentages of the following three groups of grain sizes were determined: <4 μm (clay), 4–63 μm (silt), and >63 μm (sand).

3. Results and discussion

3.1. Sediment characteristics

The studied sediments are mainly composed of clay and silt, and the percentages of fine fraction (clay + silt) are >90% for most of the samples (Table 1). Sediments of the stations close to the mouth

of the bay, however, have relatively less clay but more silt than those of the other stations. Spatially, the CaCO₃ content is more variable than TOM. The TOM content varies from 7.1% to 12.6% of the dry sediment weight with an average of 10.1%; the CaCO₃ content varies from 4.1% to 12.2% of the dry sediment weight with an average of 7.6% (Table 1). The highest contents of TOM and CaCO₃ are recorded at the same sampling station (Table 1).

3.2. Total concentration of metals

Among all the analyzed metals in this study, Mn is the most abundant one with a mean total content of 837 μg g⁻¹ (Table 3). Ba is the second most abundant element, reaching a mean total content of 361 μg g⁻¹. The other two metals with mean total content higher than 100 μg g⁻¹ are Sr and Zn, 209 and 113 μg g⁻¹, respectively. The mean total content of Pb and U is 45.7 and 3.53 μg g⁻¹, nearly twice as high as that of Cu (20.8 μg g⁻¹) and Mo (1.83 μg g⁻¹), respectively. Co and Sc present similar mean total content, 12.7 and 12.0 μg g⁻¹, respectively. The mean total content of Cd is only 0.049 μg g⁻¹, an order to several orders of magnitude lower than those of the other eleven metals. According to the research carried out in August 1996 in the region around stations 3 and 4 of this study, the mean total content of Cd, Cu, Pb and Zn in the surface sediments of Daya Bay was 0.029 μg g⁻¹, 25 μg g⁻¹, 23 μg g⁻¹ and 89 μg g⁻¹, respectively (Qiu and Wang, 1997), which are all lower than the corresponding value of this study especially for Pb. This indicates that Daya Bay has accumulated a considerable amount of these metals from anthropogenic sources during the period of about 10 years.

In the surface sediments of Daya Bay, the mean total contents of Mn, Ni, Pb, U and Zn are clearly higher with respect to the average crust values; the mean total contents of Co, Cu, Mo and Sc are comparable to the average crust values; the mean total contents of Ba, Cd and Sr are much lower than the average crust values (Table 3).

Table 2

Summary of the BCR sequential extraction protocol. For each sample, the wet weight corresponding to approximately 0.5 g dry weight based on water content measurements was used. 0.1 g residue (dry weight) from step III was used to measure Fraction 4.

Step	Fraction	Components extracted	Extraction reagent	Extraction method
I	Fraction 1, acid soluble	Exchangeable and bound to carbonates	20 ml 0.11 M HOAc	Shaking at 22 ± 5 °C for 16 h
II	Fraction 2, reducible	Bound to Fe/Mn oxides	20 ml 0.5 M NH ₂ OH · HCl (adjusted to pH 1.5 with HNO ₃)	Shaking at 22 ± 5 °C for 16 h
III	Fraction 3, oxidizable	Bound to organic matter and sulfides	5 ml 8.8 mol l ⁻¹ H ₂ O ₂ (adjusted to pH = 2.0 with HNO ₃)/another 5 ml 8.8 mol l ⁻¹ H ₂ O ₂ (adjusted to pH = 2.0 with HNO ₃)/25 ml 1 mol l ⁻¹ NH ₄ OAc (adjusted to pH 2.0 with HNO ₃)	Digesting at room temperature for 1 h with occasional manual shaking, then cover the tube and heat at 85 ± 2 °C for 1 h, and then remove the cover and reduce the volume to a few milliliters/cover the tube and heat at 85 ± 2 °C for 1 h, and then remove the cover and reduce the volume to near dryness/shaking at 22 ± 5 °C for 16 h
IV	Fraction 4, residual	Metals within lithogenic minerals	8 ml the mixture of concentrated HF, HNO ₃ and HClO ₄ (5:2:1)	Heat at a temperature of 90–190 °C for 16 h

Table 3
Metal content extracted from each step of the BCR sequential extraction procedure and the sum of content from all steps. The average upper continental crust values were also shown for comparison purpose. Content unit is $\mu\text{g g}^{-1}$ for all elements.

		Ba	Cd	Co	Cu	Mn	Mo	Ni	Pb	Sc	Sr	U	Zn
Fraction 1	Sta. 1	0.72	nd ^a	0.84	0.25	394	0.011	1.27	2.23	0.013	60.3	0.044	0.92
	Sta. 2	1.19	0.008	0.94	0.27	467	0.012	1.46	2.64	nd	78.1	0.064	3.22
	Sta. 3	1.69	0.010	0.51	0.65	309	0.028	3.19	1.91	0.063	61.3	0.127	0.76
	Sta. 4	0.63	nd	1.46	0.59	336	nd	1.82	3.05	0.047	116	0.102	2.02
	Sta. 5	0.58	nd	0.72	0.24	345	0.017	1.34	0.85	0.042	72.8	0.069	2.23
	Sta. 6	0.58	0.061	0.99	1.34	418	nd	2.51	2.66	0.037	72.9	0.061	7.44
	Sta. 7	0.58	nd	0.72	0.33	300	nd	1.66	1.98	0.053	85.6	0.072	1.18
	Sta. 8	1.37	nd	0.52	0.36	585	0.025	2.22	2.04	0.075	125	0.057	1.30
	Sta. 9	0.82	nd	0.66	0.34	517	nd	1.74	2.08	0.061	69.0	0.037	0.94
	Mean	0.91	0.009	0.82	0.49	408	0.010	1.91	2.16	0.043	144	0.070	2.22
	SD	0.41	0.020	0.29	0.35	98	0.011	0.63	0.63	0.024	177	0.028	2.11
	CV (%)	45	222	35	71	24	108	33	29	56	123	40	95
Fraction 2	Sta. 1	1.81	nd	1.85	0.59	107	nd	1.52	13.5	0.068	8.47	0.055	7.24
	Sta. 2	2.07	0.008	1.83	0.75	120	0.014	2.04	14.6	0.028	10.1	0.060	13.2
	Sta. 3	1.68	0.021	1.42	4.05	98.4	nd	2.39	16.1	0.017	31.6	0.056	12.3
	Sta. 4	1.41	0.014	1.75	1.52	86.3	0.012	1.48	16.2	0.022	10.1	0.087	10.7
	Sta. 5	2.01	nd	1.57	0.52	110	0.012	1.45	12.3	0.023	9.24	0.096	6.67
	Sta. 6	2.47	0.015	1.63	3.72	141	0.012	1.93	15.3	nd	11.3	0.068	20.2
	Sta. 7	1.53	0.019	1.62	1.18	120	nd	1.69	13.7	nd	12.9	0.086	9.11
	Sta. 8	2.79	nd	1.73	1.76	196	nd	1.98	16.7	nd	15.5	0.046	11.1
	Sta. 9	1.38	0.008	1.64	1.04	147	nd	1.76	13.6	nd	10.9	0.043	7.92
	Mean	1.91	0.010	1.67	1.68	125	0.006	1.80	14.7	0.018	13.3	0.066	10.9
	SD	0.48	0.008	0.13	1.32	33	0.007	0.31	1.5	0.022	7.2	0.019	4.1
	CV (%)	25	80	8	78	26	119	17	10	126	54	29	38
Fraction 3	Sta. 1	2.76	nd	1.09	0.32	33.4	0.11	2.28	1.33	0.10	1.26	0.34	3.92
	Sta. 2	2.03	0.011	1.21	0.48	46.7	0.10	2.99	1.26	0.16	1.58	0.53	6.08
	Sta. 3	2.19	0.008	1.10	2.85	38.0	0.20	3.42	2.35	0.19	2.92	0.75	7.19
	Sta. 4	1.97	0.025	1.25	0.67	39.3	0.26	2.67	1.22	0.14	1.31	0.87	9.39
	Sta. 5	2.59	0.011	1.11	0.54	42.5	0.17	2.55	0.94	0.16	1.24	0.52	4.14
	Sta. 6	2.50	0.014	1.33	2.18	72.5	0.15	4.58	1.50	0.29	1.81	0.69	9.52
	Sta. 7	2.49	nd	1.33	0.70	65.3	0.11	3.87	1.29	0.25	1.97	0.68	5.46
	Sta. 8	1.52	0.018	1.14	0.91	62.3	0.09	3.22	1.55	0.23	1.99	0.48	4.71
	Sta. 9	2.14	0.008	1.20	0.77	54.5	0.08	3.13	1.43	0.19	1.66	0.44	4.65
	Mean	2.24	0.011	1.20	1.05	50.5	0.14	3.19	1.43	0.19	1.75	0.59	6.12
	SD	0.38	0.008	0.09	0.87	13.7	0.06	0.71	0.39	0.06	0.53	0.17	2.14
	CV (%)	17	76	8	83	27	43	22	27	30	30	29	35
Fraction 4	Sta. 1	412	0.023	8.53	14.8	236	1.43	22.6	25.1	11.8	68.5	3.00	88.5
	Sta. 2	370	0.020	9.37	16.7	246	1.49	25.7	26.7	12.7	54.2	2.86	95.6
	Sta. 3	326	0.031	7.54	20.6	228	2.00	21.6	29.8	10.8	43.6	3.29	86.9
	Sta. 4	375	0.012	7.50	15.5	252	2.43	21.9	23.3	11.2	58.2	3.47	80.9
	Sta. 5	338	0.014	8.43	14.4	216	1.62	23.1	21.3	9.60	49.9	2.17	82.6
	Sta. 6	349	0.015	9.78	20.8	267	1.76	26.5	29.3	12.6	41.9	2.58	103
	Sta. 7	370	0.013	9.89	16.7	280	1.52	25.5	27.4	12.2	51.3	2.58	98.3
	Sta. 8	315	0.029	9.71	19.2	282	1.40	24.4	34.3	12.1	41.1	2.74	101
	Sta. 9	348	0.022	10.3	19.1	274	1.39	27.3	29.9	12.8	45.8	2.58	105
	Mean	356	0.020	9.01	17.5	253	1.67	24.3	27.5	11.8	50.5	2.81	93.5
	SD	29	0.007	1.04	2.5	24	0.35	2.1	3.9	1.1	8.9	0.40	9.0
	CV (%)	8	35	12	14	9	21	9	14	9	18	14	10
Sum	Sta. 1	417	0.023	12.3	16.0	770	1.56	27.7	42.2	12.0	139	3.44	101
	Sta. 2	375	0.047	13.3	18.2	880	1.62	32.2	45.2	12.9	144	3.51	118
	Sta. 3	332	0.070	10.6	28.2	673	2.23	30.6	50.2	11.1	691	4.22	107
	Sta. 4	379	0.051	12.0	18.3	714	2.70	27.9	43.8	11.4	186	4.53	103
	Sta. 5	343	0.025	11.8	15.7	714	1.82	28.4	35.4	9.83	133	2.86	95.6
	Sta. 6	355	0.105	13.7	28.0	899	1.92	35.5	48.8	12.9	128	3.40	140
	Sta. 7	375	0.032	13.6	18.9	765	1.64	32.7	44.4	12.5	152	3.42	114
	Sta. 8	321	0.047	13.1	22.2	1125	1.52	31.8	54.6	12.4	184	3.32	118
	Sta. 9	352	0.038	13.8	21.3	993	1.47	33.9	47.0	13.1	127	3.10	118
	Mean	361	0.049	12.7	20.8	837	1.83	31.2	45.7	12.0	209	3.53	113
	SD	28	0.024	1.0	4.4	141	0.38	2.6	5.1	1.0	172	0.49	13
	CV (%)	8	50	8	21	17	21	8	11	8	82	14	11
UCC ^b	550	0.098	10	25	600	1.5	20	20	11	350	2.8	71	

^a nd means not detected.

^b Average concentrations of the upper continental crust (Taylor and McLennan, 1995).

Based on their coefficients of variation (CVs), the total contents of Cd, Cu, Mo and Sr are found to vary significantly with sites, while total contents of other elements are slightly varied (Table 3). For nearly half of the 12 studied elements, including Cu, Pb, Sc, U, and

Zn, their total contents are lowest at station 5, which is the farthest station from the coastline. The maxima of different elements' total content are recorded at all sampling stations, except for stations 2 and 5. These facts show a clue that human activities may

influence the spatial distribution of some metals in the surface sediments of Daya Bay, but the extent is not considerable. It is likely that the total content of Cd being highest at station 6 is caused by anthropogenic input, because this station is located in the most extensive aquacultural region in the northwest part of Daya Bay and surrounded by many factories.

The National Standard of China (NSC) GB18668-2002 (SEPA, 2002) has defined three grades of marine sediment, in which the content of some heavy metals is regarded as parameters used to classify marine sediment quality (Table 4). According to this criterion, the first class quality is suitable for mariculture, nature reserves, endangered species reserves, and leisure activities such as swimming; the second class quality can be used for industry and tourism sites; and the third class can only be used for harbors. In Hong Kong, a stricter criterion has been used to distinguish sediment quality (Lau et al., 1993). The contents of Cd, Cu, Pb and Zn in all samples are lower than the upper limit of the first class criteria of NSC GB18668-2002. The contents of Cu at stations 3, 6, 8 and 9, and Ni, Pb and Zn at all stations are, to some extent, higher than the values which are regarded as the upper limit of the desired quality for fairly clean sediments, but lower than the threshold values which are used to indicate moderately contaminated sediments (Table 4). According to their corresponding Effects Range—Low (ERL) guideline values (Long et al., 1995), the contents of Cd, Cu and Zn at all stations are lower enough and probably could not cause adverse effects on the Daya Bay biota (Table 4). The Ni is higher than its ERL guideline value at all stations, but lower than its Effects Range—Median (ERM) guideline value. Lead is lower than its ERL guideline value at stations 1, 2, 4, 5 and 7 whereas at the other stations it is a bit higher.

3.3. Metal speciation

The concentrations of metals measured in each step of extraction are listed in Table 3. The distribution in percent (%) obtained for each metal in different extraction fractions is shown in Fig. 2. The studied metals take on different speciation patterns, and some of them show significant spatial variation, especially for Cd. Along a distribution of the four fractions, except for Mn and Sr, they are basically retained in the residual fraction of the sediments, which account for ~43.2–98.6% of their total content on average.

Based on the mean fraction values of the nine samples, the studied 12 elements could be classified into five groups. For group

1, which includes Ba and Cd, the residual fraction was the most abundant fraction, followed by oxidizable, reducible and acid soluble fraction in sequence, namely the percentage of the four fractions took on a relative order of Fraction 4 > 3 > 2 > 1; group 2 includes Co, Cu and Zn, and the percentage of the four fractions took on a relative order of Fraction 4 > 2 > 3 > 1 for these elements; group 3 includes Mo, Ni, Sc, and U, and the percentage of the four fractions took on a relative order of Fraction 4 > 3 > 1 > 2 for these elements; group 4 includes Mn and Sr, and the percentage of the four fractions took on a relative order of Fraction 1 > 4 > 2 > 3 for these elements; group 5 includes only Pb, and the percentage of the four fractions took on a relative order of Fraction 4 > 2 > 1 > 3 for this element.

For most of the studied metals, their percentage in Fractions 1 to 3 varies greatly from one sampling station to another as showed by the CVs, especially in Fraction 1. The CVs of their percentage in Fraction 1 are >50% for half of the 12 metals.

3.3.1. Ba and Cd

On average, ~99% of Ba is associated with the residual fraction, which is comparable to Sc and higher than other elements. Ba in Fractions 1 to 3 accounts for <1% of its total content at all sampling stations. This indicates that Ba mobility in the Daya Bay surface sediment is very low, and only a slight amount of it can be in equilibrium with the water body. Spatial difference of Ba in the residual fraction is not significant (Fig. 2).

Cd speciation is found to be highly variable, perhaps because it is a typical anthropogenic element and mostly enters the aquatic environment through the discharge of industrial effluents (Fig. 2). On average, ~57% of Cd is mainly distributed among the non-residual fractions, which makes it the third most mobile element after Mn and Sr. Compared to most of other metals, each fraction of Cd takes on apparent differences between samples. ~0–58% of its total content is measured in the first step of extraction with a mean of ~10%, and ~0–59%, ~0–49% and ~14–100% are found in the second, the third and the fourth stages with mean values of ~19%, ~22% and ~49%, respectively. A large proportion of Cd deposited in the sediment can be remobilized as a result of the mineralization of organic matter under oxic conditions (Petersen et al., 1995).

3.3.2. Co, Cu and Zn

These three elements are detected in all of the four operationally defined sediment phases. The highest concentrations of these elements are recorded in the residual fraction at all sampling stations, on average accounting for 70.8%, 85.9% and 83.2% of the total content of Co, Cu and Zn, respectively (Fig. 2). The most abundant values of Co, Cu and Zn in the non-residual fractions are observed at the second extraction step, and on average account for 13.3%, 7.4% and 9.5% of their total concentrations, respectively. Co and Zn in Fraction 1 and Cu in Fraction 2 are spatially more variable than in the other three fractions.

A number of previous studies on different kinds of sediments have showed that non-residual fractions of Cu are mainly associated with the oxidizable phase, occurring as organically complexed metal species (e.g. Pardo et al., 1993; Li et al., 2007). This is because Cu shows high affinity with humic substances, which are a fraction of natural organic matter chemically active in complexing such metals (Pempkowiak et al., 1999).

In this study, the non-residual fractions of Cu show a different pattern, perhaps owing to the influence of early diagenetic processes. It was reported that under an oxic water column, as that of Daya Bay, a significant fraction of the Cu reaching the sediment surface may be returned to the overlying water column by mineralization of the host organic material at the surface and in the oxic

Table 4
The metal threshold values of some different criteria used to distinguish marine sediment quality ($\mu\text{g g}^{-1}$).

	Cd	Cu	Ni	Pb	Zn	Reference
Class I	0.5	35		60	150	SEPA, 2002
Class II	1.5	100		130	350	SEPA, 2002
Class III	5	200		250	600	SEPA, 2002
Target ^a	0.4	20	20	35	75	Lau et al., 1993
Trigger ^b	1.0	55	35	65	150	Lau et al., 1993
Action ^c	1.5	65	40	75	200	Lau et al., 1993
ERL guideline ^d	1.2	34	20.9	47	150	Long et al., 1995
ERM guideline ^e	9.6	270	51.6	218	410	Long et al., 1995

^a Target indicates the desired quality for fairly clean sediment that is close to background levels.

^b Trigger indicates that the sediment is moderately contaminated.

^c Action indicates heavily polluted sediments.

^d ERL (Effects Range—Low) guideline values indicate concentrations below which adverse effects on biota are rarely observed.

^e ERM (Effects Range—Median) guideline values indicate concentrations above which adverse effects on biota are frequently observed.

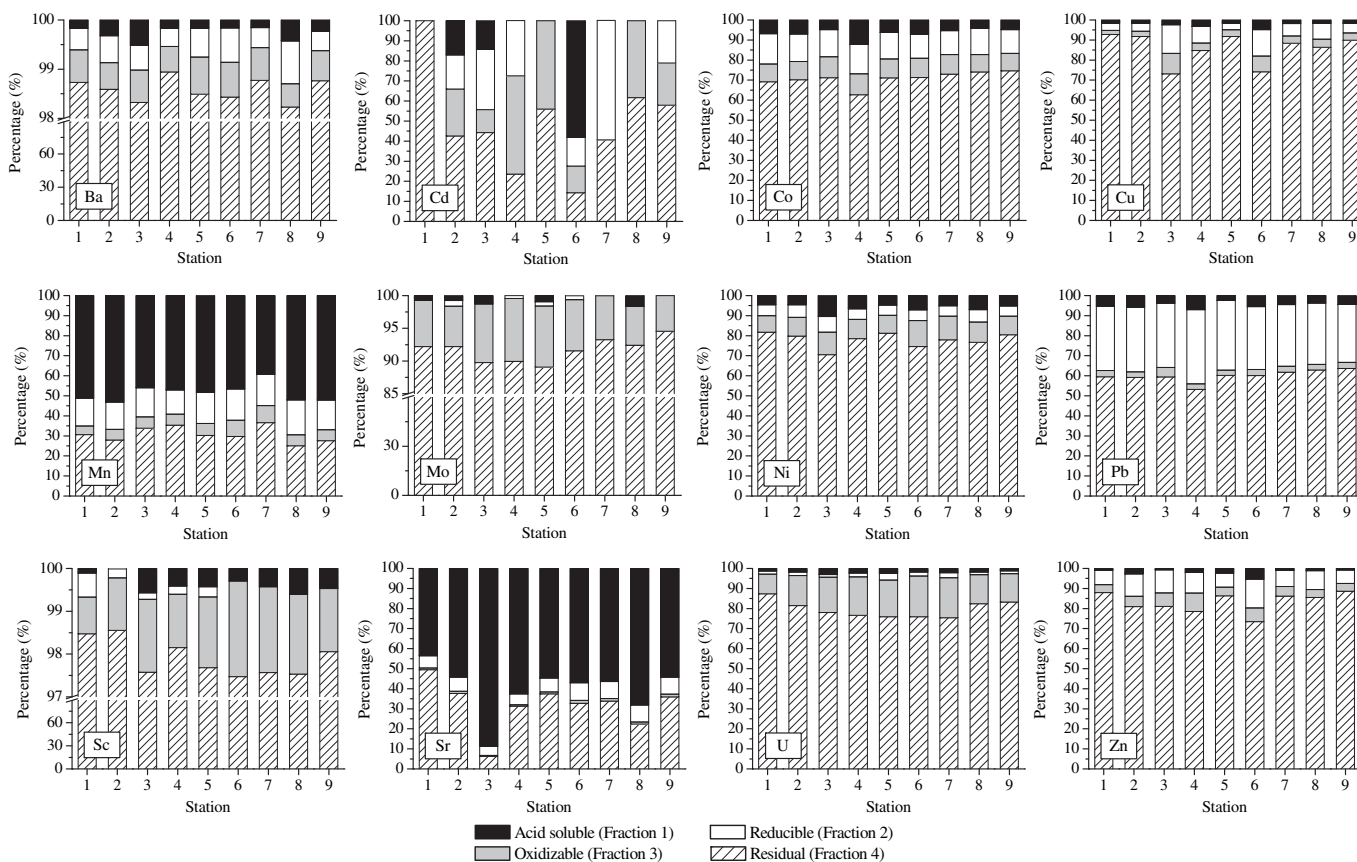


Fig. 2. The distribution of metals in different geochemical phases of sediments collected from Daya Bay. Their corresponding content is given in Table 3.

upper layers of the sediment (Petersen et al., 1995). A smaller fraction of sedimentary Zn may be remobilized for the same reason (Petersen et al., 1995). With continuing diagenesis, Cu and Zn will be released further as a result of microbial oxidation of the organic substrate (Jones and Turki, 1997).

Unlike that of Cu and Zn, under oxic conditions Co was removed from the water phase by co-precipitation and/or adsorption on the freshly formed hydrous ferric oxides; the remobilization of Co from sediment to water occurred under anoxic conditions and soon stopped when the water phase became oxic (Petersen et al., 1995).

3.3.3. Mo, Ni, Sc and U

The predominant proportions of Mo and Ni, averaging to 92% and 78% of their total contents, are present in the residual fraction, which is in agreement with the results of some other studies (e.g. Martin et al., 1998; Yuan et al., 2004). An even higher proportion of total Sc, ranging from 97.5% to 98.6% with a mean of 97.9%, is present in the residual fraction. The speciation patterns of Mo and Sc show a considerable spatial variation. For Sc, only at four of the nine sampling stations it is detected in all the four operationally defined sediment phases. For Mo, only at stations 2 and 5 it is detected in all the four operationally defined sediment phases.

Unlike some river sediments where the majority of the total U was associated with the non-residual fractions (Martínez-Aguirre et al., 1995; Martin et al., 1998), on average ~80% of the total U in the Daya Bay surface sediments is present in the residual fraction. Co-precipitation with amorphous ferromanganese oxyhydroxides is the main process of U incorporation from the water column into the sediment particles (Martínez-Aguirre et al., 1995). The waste discharge from the operation of fertilizer industries was found to be

an anthropogenic source of the enhanced U in sediments (Martínez-Aguirre et al., 1995). In Daya Bay, the waste discharge from nuclear power plants may be a possible anthropogenic source of the sedimentary U, for the total content of U at stations 3 and 4, the two stations being located closest to the two nuclear plants, is clearly higher than at the other stations (Table 3).

3.3.4. Mn and Sr

As observed by many other researchers (e.g. Tack and Verloo, 1995; Yuan et al., 2004; Naimo et al., 2005), for all the samples studied in this work, a large proportion of total Mn, accounting for 39.2–53.1% of its total content with an average of 48.4%, is found in the acid soluble fraction (Fig. 2). The percentage of Mn in the residual fraction is about twice that of it in the reducible fraction and five times that of it in the oxidizable fraction.

The Mn extracted in acid soluble fraction could come from the dissolution of Mg/Ca carbonates, as Mn^{2+} can substitute for Mg^{2+} as well as Ca^{2+} in carbonate minerals, the more so for Mg in dolomite than for Ca in calcite (Shan and Chen, 1993; Arunachalam et al., 1996). Specific adsorption of Mn at the surface of calcite is also possible (Gleyzes et al., 2002). Tessier et al. (1979) concluded from a study on sediments that the Mn found in this fraction was in a reduced state and, therefore, was not derived from a partial attack of Mn oxides.

Like Mn, the content of Sr is highest in the acid soluble fraction and on average accounts for about 60% of its total content (Fig. 2). Up to 88.7% of Sr is associated with this fraction at station 3. The acid soluble fraction represents the total of the ion-exchangeable and carbonate components of the sediment matter. Xu and Marcantonio (2004) reported that ~16% of Sr in the exchangeable and carbonate

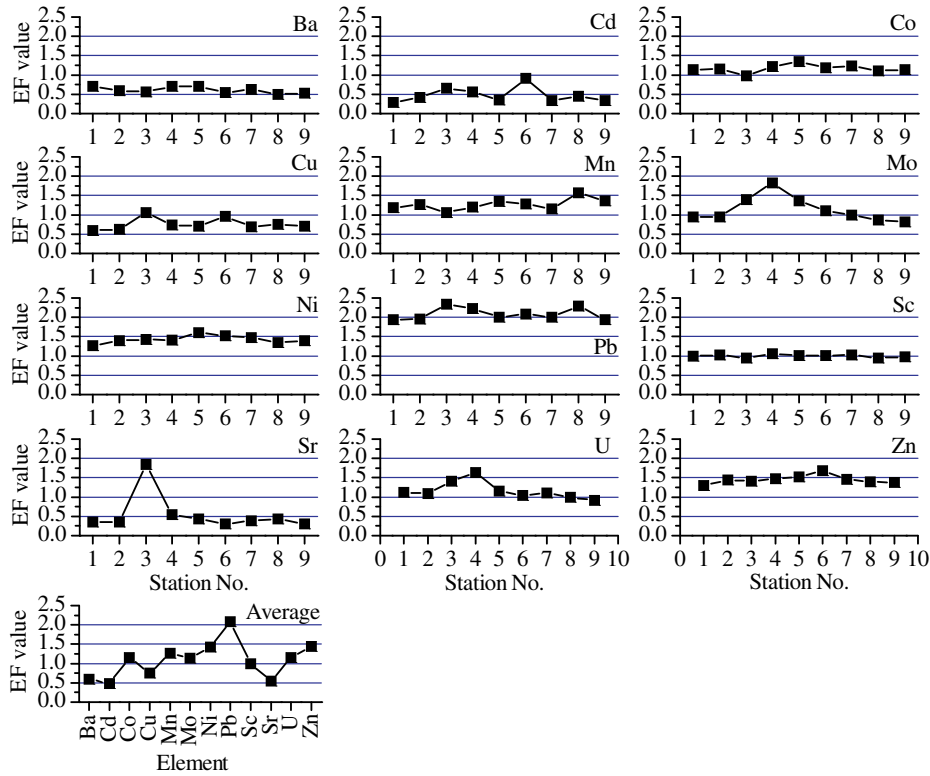


Fig. 3. The EF values of 12 studied metals in the Daya Bay surface sediments.

components can be released by de-ionized water for a particulate sample collected from the Mississippi River mixing zone. Their work provided a minimum baseline for the exchangeable fraction since seawater has higher ionic strength than de-ionized water, and then an even higher proportion of exchangeable Sr is expected.

The Sr associated with Fe/Mn oxides is significantly lower than the Sr associated with the exchangeable and carbonate fraction. It comprises only ~ 10% of the total non-residual fractions on average. The percentage of Sr in the oxidizable fraction is even lower, and only accounts for 0.4–1.4% of its total content with an average of 1.0%. A study by Andersson et al. (1994) showed that Fe/Mn oxyhydroxides can trap Sr as they form; Xu and Marcantonio (2004) reported that carbonates play a comparable, or more important, role as a carrier phase for Sr in particles, and this is proved again by the data of this study.

The fraction composition of Sr shows a significant spatial variation, while that of Mn shows no significant spatial variation (Fig. 2).

3.3.5. Pb

Lead is highly toxic to the environment. In the areas influenced by extensive human activities, a considerable proportion of Pb in the environment is of anthropogenic origin, because it is an important additive that has been widely used in many products. The speciation of Pb shows no significant spatial variation in the Daya Bay surface sediments, indicating a non-point source input feature (Fig. 2). The residual fraction of Pb accounts for 53.2–63.6% of its total content with an average of 60%. For the Pb in non-residual fractions, a major portion is bound to the Fe/Mn oxides with comparable amounts associated with the acid soluble and oxidizable fractions. The fact that Pb can form stable complexes with Fe and Mn dioxide (Ramos et al., 1994) may be the reason why reducible Pb is more abundant than the other two non-residual

fractions of Pb. The reducible Pb predominating in non-residual fractions has been reported by many researchers (e.g. Li et al., 2001; Ip et al., 2007). The content of Pb measured in Fraction 1 is very low and only accounts for 2.4–7.0% of its total content with an average of 4.7%, limiting its potential toxicity as pollutant in Daya Bay.

3.4. Metal enrichment and potential risk in surface sediments

The enrichment factor (EF) for each element was calculated to evaluate anthropogenic influences on heavy metals in sediments using the following formula (Selvaraj et al., 2004):

$$EF = \frac{(C_x/C_{Al})_S}{(C_x/C_{Al})_{UCC}}$$

where C_x and C_{Al} denote the concentrations of elements x and Al in the samples of interest (S) and the upper continental crust (UCC) (Taylor and McLennan, 1995).

Generally, an EF value of about 1 suggests that a given metal may be entirely from crustal materials or natural weathering processes (Zhang and Liu, 2002). Nevertheless, a slight positive deviation of EF value from unity may not arise from anthropogenic activities, for the natural difference in elemental composition between a pristine sediment and the reference Earth's crust used in

Table 5
Criteria of risk assessment code (Perin et al., 1985).

Grade	Exchangeable and bounded to carbonate metal (%)	Risk
I	<1	No risk
II	1–10	Low risk
III	11–30	Medium risk
IV	31–50	High risk
V	>50	Very high risk

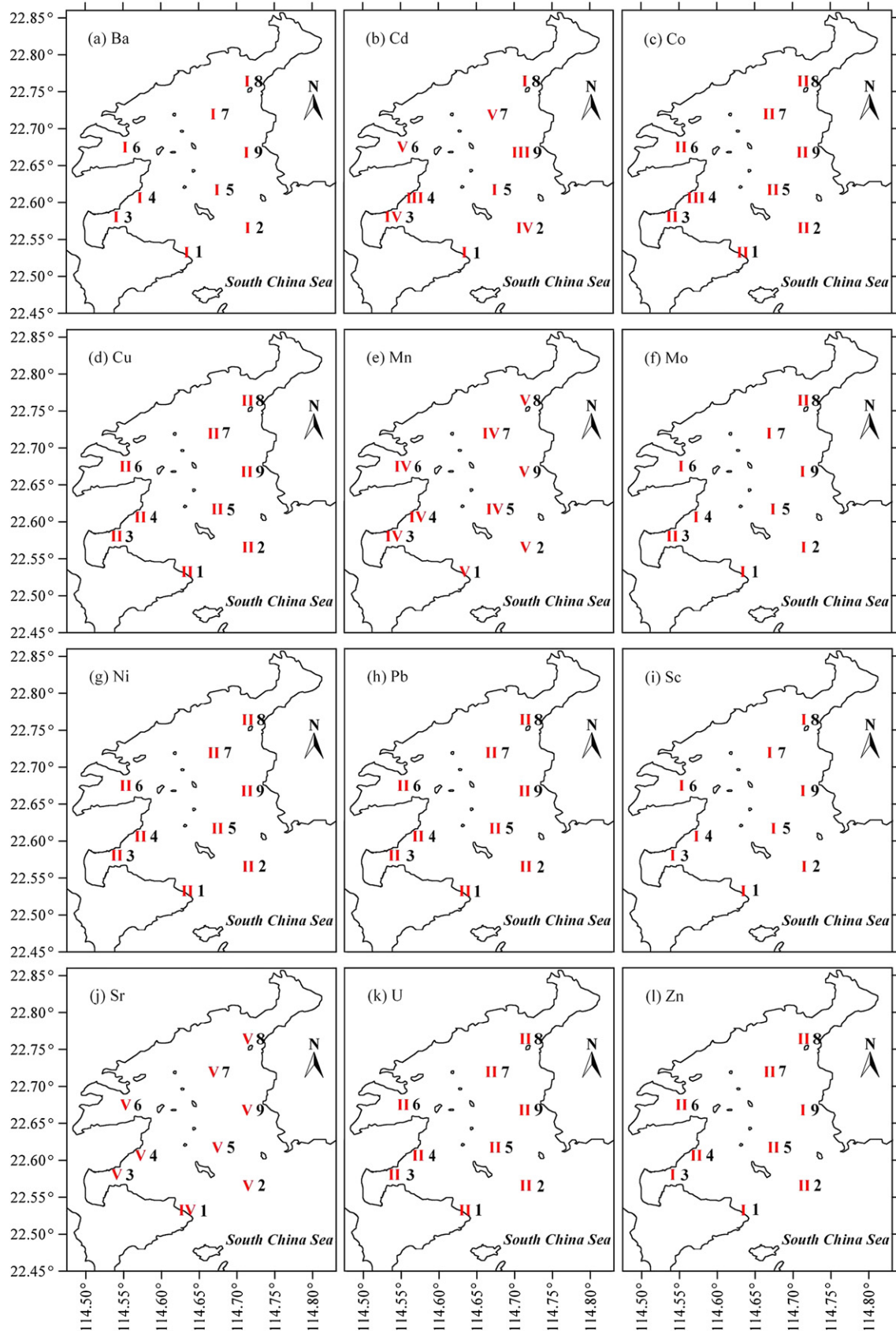


Fig. 4. Risk assessment result.

EF calculation could also cause it. An EF value of >1.5 suggests that a significant portion of metal is delivered from non-crustal materials, or non-natural weathering processes, so anthropogenic sources become an important contributor (Feng et al., 2004). Taken as a whole, the EFs of the 12 studied metals in surface sediments of Daya Bay decreased in the sequence of $Pb > Zn > Ni > Mn > Co > U > Mo > Sc > Cu > Ba > Sr > Cd$ (Fig. 3). Except at station 4, the EFs of Pb are all >1.5 at the other eight stations with the highest value of 2.09 being recorded at station 8; the $EF > 1.5$ is only recorded at station 3 for Sr, at station 4 for Mo and U, at stations 5 and 6 for Ni and Zn, and at station 8 for Mn; No $EF > 1.5$ is recorded at all sampling stations for the other metals. The EFs of this study give a clue that anthropogenic input is not a major source of the studied metals in the Daya Bay surface sediments and causes no evident environmental pollution except for Pb.

Metal speciation is of critical importance to their potential toxicity and mobility (Maiz et al., 2000). The metals in acid soluble fraction are considered to be the weakest bonded metals in sediments which may equilibrate with the aqueous phase, and thus become more easily bioavailable (Pardo et al., 1990). A criterion called “Risk Assessment Code (RAC)” has been used to assess the potential mobility and hazard of metal based on the percentage of exchangeable and bound to carbonate metal in sediment (e.g. Perin et al., 1985; Jain, 2004; Ghrefat and Yusuf, 2006). The standards of RAC are listed in Table 5. The results of the present study showed that Ba and Sc in the sediments at all sampling stations are in a no risk category; Cd is in a very high risk category at stations 6 and 7, in a high risk category at stations 2 and 3 and in a no risk and medium risk category at the other stations; Co is in a low risk to medium risk category; Cu, Ni, Pb and U are all in a low risk category; Mo and Zn are in a no risk to low risk category; Mn and Sr pose a high risk to very high risk to the environment according to RAC (Fig. 4).

4. Conclusions

The study reveals that the total concentrations of Ba, Co, Ni, Pb, Sc and Zn show a relatively slight spatial variation in the surface sediments of Daya Bay, indicating that they are mainly from non-point source inputs. There is a considerable spatial variation in the total concentrations of other metals, especially for Cd and Sr.

According to the National Standard of China, the total concentrations of Cd, Cu, Pb and Zn are fairly low at present and suitable for mariculture, nature reserves, endangered species reserves, and leisure activities such as swimming. The total concentration of Ni at some sampling stations is close to the threshold value for moderately contaminated sediment. The total concentrations of Cd, Cu and Zn are low enough and probably could not cause adverse effects on the Daya Bay biota.

A majority of the 12 studied metals can be considered immobile because of their high percentages in the residual fraction, which suggests that they are strongly bound to minerals and resistant components, and are not anthropogenically introduced into sediments. The metals that are most easily extracted in the samples analyzed are Cd, Mn, Pb and also Sr in the surface sediments of Daya Bay. On the whole, all studied metals in the sediments except for Cd, Mn and Sr have generally no risk or low risk to the environment.

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