

Baseline establishment for metals in the western Clarion-Clipperton Zone

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Abstract

Resource exploitation in the Clarion-Clipperton Zone (CCZ) is of major research interest worldwide, but its influence on the environment is poorly understood, especially due to the lack of baseline values for metals in the surrounding sediment. This work aimed to establish the baseline values of 17 metals (Ba, Ca, K, Mg, Mn, Na, Ag, As, B, Cd, Co, Cr, Cu, Hg, Ni, Pb, and Zn) using normalization, the cumulative frequency curve method considering a total of 172 samples taken from 8 multitube cores and 1 box sediment core collected in the western CCZ during the COMRA-45 cruise campaign from August to September 2017. The baseline values of the evaluated metals were as follows: 1 932 mg/kg for Ba, 29 512 mg/kg for Ca, 18 150 mg/kg for K, 17 120 mg/kg for Mg, 6 747 mg/kg for Mn, 28 546 mg/kg for Na, 0.571 mg/kg for Ag, 5.00 mg/kg for As, 94.4 mg/kg for B, 0.626 mg/kg for Cd, 104 mg/kg for Co, 76.1 mg/kg for Cr, 370 mg/kg for Cu, 0.028 mg/kg for Hg, 190 mg/kg for Ni, 27.5 mg/kg for Pb and 156 mg/kg for Zn. Our findings would fill the baseline value gap in the study area and further improve accuracy of environmental impact assessments on the impact of resource exploitation.

Key words: baseline, metals, normalization, cumulative frequency curve

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1 Introduction

Accompanied by the rapid development of modern industries, an increasing volume of heavy metals has been discharged into aquatic environment. These elements are mostly recalcitrant in the environment and thus pose considerable hazards to ecosystems and human health. Additionally, they can easily migrate across water bodies via suspended matter and sediment through adsorption and desorption. Furthermore, they can even be enriched exceeding 1 000 times via the food chain and generate adverse effects on the biota. Hence, heavy metal pollution has become a severe environmental issue of concern and attracted great attention.

Researchers have mainly focused on the distribution, speculation, source, and potential risk assessment of heavy metals in waters or sediments worldwide in addition to their influencing factors. The studied areas mainly focus on estuaries, lakes and nearshores, such as the Nile Delta in Egypt (Mandour et al., 2021); the Laucala Bay in Fuji (Pratap et al., 2020); the Swan River in western Australia (Rate et al., 2000) and the Finiss River in the Northern Territory, Australia (Taylor, 2007); the Nanhai Lake, the channel of Yellow River (Liang et al., 2009), the Changjiang River Estuary (Zhuang and Zhou, 2021), the Jiulong River or the Xiamen Bay (Lin et al., 2011, 2014), the offshore area of eastern Sanya (Zhang et al., 2018) and the Bohai Sea in China (Zhu et al., 2019); the Ganges Estuary at northeast of the Bay of Bengal in India (Chatterjee et al., 2007; Singh et al., 2017; Siddiqui and

Pandey, 2019); the Al-Karak catchment area in the southern Jordan (El-Hasan and Jiries, 2001); and the Nahr-Ibrahim River in Lebanon (Korfali and Davies, 2003). Besides, in the open ocean especially in the Clarion-Clipperton Zone (CCZ), paleoceanographic, sedimentologic, structural geology, and volcanic geology studies have broadly reported the ferromanganese formation mechanism and sediment element distribution of heavy metals, platinum group elements and rare earth elements since the 1950s (Zhang et al., 2001; Kuang et al., 2004; Yang et al., 2007a, b; Huang et al., 2014; Ren et al., 2015; Wang, 2017; Deng et al., 2018), but the research about baseline value establish in the CCZ is almost none.

The CCZ in the East Pacific Ocean is a distribution area with the greatest abundance of polymetallic nodules in the world. Currently, deep-sea mining is becoming a topic of major interest, but its environmental impact is unclear. Hence, the International Seabed Authority attaches a great amount of importance to establishing environmental baselines in the CCZ, including physical, chemical, and biological baselines, because the assessment of the environmental impact of polymetallic mining is based on various parameters of mining activities. Resuspension of sediments, desorption of metals, and migration to mesopelagic waters may occur during mining activities. Changes in the abundance and biomass of meiofauna and megafauna might occur after the bio-absorption of metals, resulting in alteration of community structure and biodiversity. Hence, the baseline values of

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metals in the CCZ are the basic data reflecting the impact of poly-metallic mining.

The baseline of certain metals (As, Co, Cr, Cu, Hg, Mn, Ni, Pb, and Zn) has been set through normalization and accumulative frequency curve methods in sediments of coastal waters and freshwaters (Singh et al., 2003; Wei and Wen, 2012; Jiang et al., 2013). However, a baseline of metals in the open ocean particularly in the CCZ, is unavailable. During the China Ocean Mineral Resources R&D Association-45 (COMRA-45) Cruise from August to September 2017, nine sediment core samples, including eight multitubes and one box-type sample, were collected in the COMRA contract and adjacent area in the western CCZ. This work aims to establish the baseline values of 17 metals (Ba, Ca, K, Mg, Mn, Na, Ag, As, B, Cd, Co, Cr, Cu, Hg, Ni, Pb, and Zn), which would fill the environmental baseline data gap and better carry out environmental impact assessments of mining exploitation.

2 Methods

2.1 Sampling

Eight sediment cores from Stations 2 to 9 were collected using a multitube sampler and one core from Station 1 by a box sampler with a plexiglass tube in COMRA's contract and its adjacent area of 8°–13°N, 153°–155°W in the western CCZ during the COMRA-45 Cruise from August to September 2017, as shown in Fig. 1.

The lengths of the sediment cores from Stations 1 through 9 were 34 cm, 26 cm, 32 cm, 30 cm, 36 cm, 30 cm, 40 cm, 46 cm and 52 cm, respectively. The sediment cores were sliced into 1 cm intervals from top to 2 cm depth and 2 cm intervals from 2 cm depth to the base using stainless steel cutters. A total of 172 samples were transferred into polyethylene storage bags and kept frozen

for further laboratory analysis.

2.2 Chemical analysis

Samples were freeze-dried using a vacuum freeze dryer (LYO-VAC GT2, Leybold-Heraeus, Germany) and ground with a mortar grinder (RM200, Retsch, Germany) to sift through a 200-mesh nylon sieve. Aliquots of 0.1 g of the ground samples were digested by a microwave digestion instrument (MARS6, CEM, USA) with a mixture of 6 mL subboiling distilled nitric acid (trace purity) and 2 mL hydrofluoric acid for 30 min at 180°C and 800 PSI. The resulting mixture was then added to 1 mL perchloric acid and steamed near dry at 150°C by an acid catcher (ZLT-GSB-20G, China). The residue was redissolved in 2 mL 1% nitric acid (trace purity), filtered, and diluted to 10 mL with Milli-Q water, after which 16 metals (Ba, Ca, K, Mg, Mn, Na, Ag, As, B, Cd, Co, Cr, Cu, Ni, Pb, and Zn) were measured using inductively coupled plasma mass spectrometry (ICP-MS, Agilent, USA). The solution was diluted to obtain three groups of different multiples (400 times, 10 times and no dilution) for measurement according to their metal content. Hg was digested with a mixture of 2 mL nitric acid (trace purity) and 6 mL hydrochloric acid, and was measured using atomic fluorescence photometer (AFS, Beijing Titan, China) according to General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China, Standardization Administration of China (2008).

Grain size was measured according to General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China (2007). An appropriate amount of wet sample with 100 mL Milli-Q water was added to 10 mL 30% hydrogen peroxide solution, reacted at room temperature for 24 h to remove the organic matter. Then, 30 mL 10% hydrochloric acid was added to the liquor to remove the carbonate component after another 24 h at room temperature. The residue was then added to 10 mL 0.5 mol/L sodium hexametaphosphate, dispersed by ultrasonic oscillation for 10 min and measured by a laser particle size analyzer (Mastersizer 2000, Malvern, UK) with a relative error less than 3% for repeated measurement.

Certified reference materials GBW07316 and GBW07314 from the Center for Standard Reference of China were processed employing the same process as outlined above to ensure analytical accuracy. The measurement results, recoveries, accuracies of GBW07316 and GBW07314 and detection limits of methodology are shown in Table 1. Milli-Q water (18.2 M Ω -cm, 25°C) was used throughout the analysis. All the other reagents were of guaranteed reagent or better.

2.3 Baseline calculation

The baseline calculation includes normalization, statistical methods, and geochemical comparison methods (Colizza et al., 1996; Schiff and Weisberg, 1999; Matschullat et al., 2000; Newman and Watling, 2007; Teng et al., 2009; Wei and Wen, 2012; Karim et al., 2015; Niu et al., 2019; Sun et al., 2019; Wang et al., 2020). Most researches were about trace metals, but O'Donnell et al. (2004) established geochemical baseline data including constant elements (Fe, Mn, Ti) and trace elements (Sb, As, Ba, Cd, Cr, Co, Cu, Pb, Mo, Ni, Sn, U, V, Zn) for the urban area of Kingston-upon-Hull. Karim et al. (2015) and Teng et al. (2009) determined geochemical baseline for constant element Fe in Pakistan using cumulative frequency curves and that in South China by normalization respectively. Therefore, we adopted normalization and cumulative frequency curves to estimate the baseline value of 17 metals including constant and trace elements.

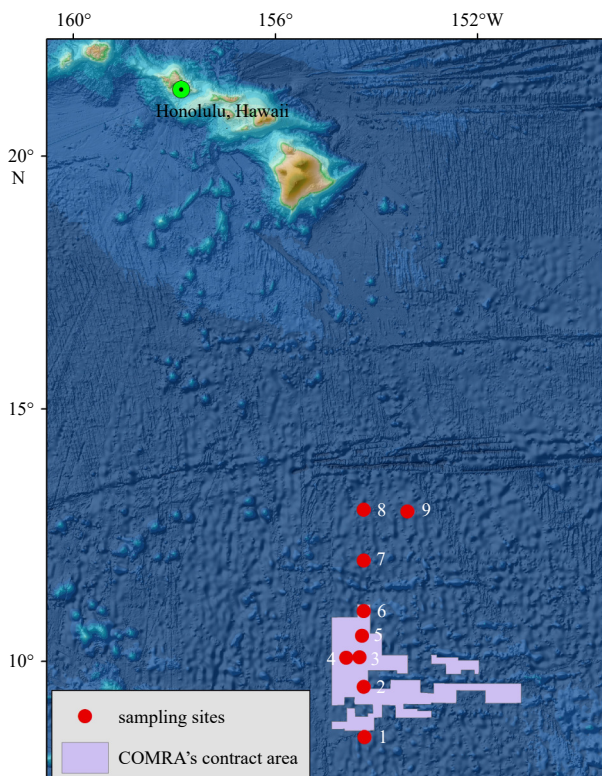


Fig. 1. Sampling stations. COMRA: China Ocean Mineral Resources R&D Association.

Table 1. Measurement, recovery, accuracy of GBW 07316 and GBW 07314 and detection limit

		Ba content	Ca content	K content	Mg content	Mn content	Na content	Ag content	As content	
GBW 07316	Standard value/(mg·kg ⁻¹)	2 500±200	161 429±4 286	13 360±996	12 240±420	3 099±155	27 823±1 039	–	4.60±0.50	
	Measurement 1/(mg·kg ⁻¹)	2 664	162 683	12 763	12 236	3 012	27 219	0.157	4.27	
	Measurement 2/(mg·kg ⁻¹)	2 325	159 215	13 827	12 065	3 212	28 297	0.146	4.31	
	Measurement 3/(mg·kg ⁻¹)	2 600	161 092	12 700	12 503	3 049	27 476	0.143	4.40	
	Measurement 4/(mg·kg ⁻¹)	2 532	160 584	14 046	12 056	3 146	28 324	0.167	4.82	
	Measurement 5/(mg·kg ⁻¹)	2 394	162 803	13 342	12 124	2 951	27 039	0.132	4.31	
	Recovery/%	93.0–107	98.6–101	95.1–105	98.5–102	95.2–104	97.2–102	–	92.8–105	
	RSD/%	5.6	0.9	4.6	1.5	3.4	2.2	8.9	5.2	
GBW 07314	Standard value/(mg·kg ⁻¹)	425±20	30 786±1 714	20 579±1 162	15 000±480	744±31	12 465±1 039	–	10.3±1.4	
	Measurement 1/(mg·kg ⁻¹)	414	30 867	21 469	14 690	722	11 907	0.503	10.1	
	Measurement 2/(mg·kg ⁻¹)	435	29 397	21 242	14 559	764	12 483	0.495	9.68	
	Measurement 3/(mg·kg ⁻¹)	420	30 015	19 959	14 546	737	12 378	0.505	8.94	
	Measurement 4/(mg·kg ⁻¹)	420	31 682	20 414	15 208	761	12 795	0.540	11.2	
	Measurement 5/(mg·kg ⁻¹)	412	29 979	19 679	15 205	723	13 059	0.502	9.65	
	Recovery/%	97.0–102	95.5–103	95.6–104	97.0–101	97.0–103	95.5–105	–	86.8–109	
	RSD/%	2.1	2.9	3.8	2.3	2.7	3.5	3.5	8.4	
	Average recovery/%	100	99.3	100	99.3	99.4	100	–	96.1	
	Average RSD/%	3.9	1.9	4.2	1.9	3.1	2.8	6.2	6.8	
Detection limit/(mg·kg ⁻¹)	23.2 ^a	1 932 ^a	243 ^a	210 ^a	0.009 ^b	927 ^a	0.006 ^a	0.180 ^b		
		B content	Cd content	Co content	Cr content	Cu content	Ni content	Pb content	Zn content	Hg content
GBW 07316	Standard value/(mg·kg ⁻¹)	84±11	0.300	53±4	38±5	231±10	108±9	22±5	142±22	0.13±0.02
	Measurement 1/(mg·kg ⁻¹)	81.6	0.326	49.8	39.1	224	102	19.6	136	0.120
	Measurement 2/(mg·kg ⁻¹)	89.8	0.266	49.6	39.8	231	99.8	23.0	137	0.128
	Measurement 3/(mg·kg ⁻¹)	83.5	0.266	55.5	38.9	226	103	25.2	123	0.118
	Measurement 4/(mg·kg ⁻¹)	78.1	0.260	56.6	42.6	236	113	24.5	149	0.132
	Measurement 5/(mg·kg ⁻¹)	75.1	0.284	56.0	41.1	228	101	21.1	122	0.142
	Recovery/%	89.4–107	86.8–109	93.6–107	102–112	97.0–102	92.4–105	89.3–114	85.8–105	90.8–109
	RSD/%	6.8	9.6	6.6	3.8	2.0	5.3	10.2	8.6	7.6
GBW 07314	Standard value/(mg·kg ⁻¹)	73.0	0.200±0.040	14.2±1.2	86.0±4.0	31.0±4.0	34.3±4.0	25.0±4.0	87.0±2.0	0.048±0.012
	Measurement 1/(mg·kg ⁻¹)	73.0	0.228	15.2	83.7	33.8	32.6	25.4	86.4	0.048
	Measurement 2/(mg·kg ⁻¹)	70.7	0.212	14.6	86.1	32.3	31.2	23.6	85.2	0.042
	Measurement 3/(mg·kg ⁻¹)	69.5	0.219	14.2	87.7	31.8	32.3	22.2	87.4	0.045
	Measurement 4/(mg·kg ⁻¹)	78.5	0.212	14.3	82.6	32.8	37.0	25.8	87.3	0.049
	Measurement 5/(mg·kg ⁻¹)	75.7	0.173	13.6	85.8	30.3	31.1	21.9	88.6	0.051
	Recovery/%	95.2–108	86.6–114	96.0–107	96.0–102	97.6–109	90.6–108	87.7–103	97.9–102	87.5–106
	RSD/%	5.0	10.0	3.9	2.4	4.1	7.4	7.5	1.4	7.5
	Average recovery/%	98.9	98.9	101	103	102	95.9	99.1	96.9	98.2
	Average RSD/%	5.9	9.8	5.2	3.1	3.0	6.3	8.9	5.0	7.5
Detection limit/(mg·kg ⁻¹)	0.831 ^a	0.015 ^b	0.016 ^b	0.070 ^b	0.008 ^b	0.003 ^b	0.070 ^b	0.160 ^b	0.002 ^c	

Note: ^a Data from this study; ^b data from HY/T 147.2–2013 (State Oceanic Administration, 2013); ^c data from General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China, Standardization Administration of China (2007). RSD: relative standard deviation. – represents no data.

2.3.1 Normalization method

The normalization method selects the inert elements in the geochemical process as the standard elements through their correlation coefficient and the active metal contents. On the premise of meeting the significance level of $P < 0.05$, the inert metal that is most strongly correlated with an active metal is then selected as the standard element. A scatter diagram was made between the active and chosen standard metals, and a 95% statistical test was carried out. After eliminating the points falling outside the 95% confidence limit, the regression equation is re-established with the remaining data. The average value of the chosen standard metal of all samples is substituted into the new regression equation to obtain the baseline value of the corresponding active metal.

Inert metals, including Al, Fe, La, Li, Sc, Ti, V, Cs, and Rb,

used to establish the baseline value of 17 metals (Ba, Ca, K, Mg, Mn, Na, Ag, As, B, Cd, Co, Cr, Cu, Hg, Ni, Pb, and Zn) were also determined in this paper.

2.3.2 Cumulative frequency curve method

A cumulative frequency curve with decimal coordinates is plotted after inputting all metal contents on the x -axis and the cumulative frequency as the y -axis. The curve may have two inflection points: the lower point may represent the upper limit of natural origin metal contents, while the higher point represents the lower limit of abnormal contents (affected by human activities). The area between the two inflections may or may not be affected by human activities, or may not be related (Matschullat et al., 2000; Teng et al., 2009). In some cases, the distribution curve is approximately linear, implying that the concentration of metals

in all samples represents the range of baseline values. Beyond that, the curve may have just one inflection, indicating a lesser anthropogenic influence (Li, 2013).

The baseline value of the evaluated metals was the median content of a given metal among samples with lower concentrations than the lower inflection when the curve had one or two inflections, which was adopted in Li (2013).

3 Results

3.1 Metal contents in the sediment

The granularity of sediment (M_d) in the research area ranged from $\Phi 3.73$ to $\Phi 7.59$ with an average value of $\Phi 6.48$, indicating that the sediment was mainly coastal silt or fine silt sand. The relatively uniform sediment types minimized the effect of grain size on metals, indicating the availability of the assessed metal baselines throughout the research area.

Figure 2 shows a box chart of depicting the measured metal contents. Expressed as average value \pm standard deviation (minimum value–maximum value), the contents of 17 metals (Ba, Ca, K, Mg, Mn, Na, Ag, As, B, Cd, Co, Cr, Cu, Hg, Ni, Pb, and Zn) were (3 112 \pm 3 717) mg/kg (306–24 029 mg/kg), (37 770 \pm 27 074) mg/kg (10 630–155 453 mg/kg), (18 998 \pm 5 652) mg/kg (8 494–35 244 mg/kg), (17 038 \pm 6 643) mg/kg (1 080–43 241 mg/kg), (7 303 \pm 3 172) mg/kg (1 833–16 261 mg/kg), (31 276 \pm 8 928) mg/kg (13 815–61 383 mg/kg), (0.62 \pm 0.26) mg/kg (0.21–1.89 mg/kg), (5.91 \pm 2.26) mg/kg (3.45–16.2 mg/kg), (105 \pm 50.6) mg/kg (27.1–222 mg/kg), (0.67 \pm 0.18 mg/kg) (0.28–1.13 mg/kg),

(110 \pm 19.6 mg/kg) (60.4–179 mg/kg), (81.8 \pm 25.2) mg/kg (19.6–168 mg/kg), (404 \pm 87.1) mg/kg (218–796 mg/kg), (0.035 \pm 0.026) mg/kg (0.010–0.19 mg/kg), (204 \pm 60) mg/kg (105–458 mg/kg), (36.5 \pm 17.8) mg/kg (2.90–89.2 mg/kg), and (162 \pm 22.5) mg/kg (110–238 mg/kg), respectively. Compared with the abundance of metals in the crust of the oceanic lithosphere (Li and Yuan, 2011), the averages of the 17 metals studied in this area accumulated, excluding Co, Ni, Mg, and Cr. The enrichment factor was ordered as follows: B(52.5)>Ba(40.9)>Pb(17.4)>Ag(10.9)>K(10.6)>Cu(10.1)>Cd(8.32)>Na(6.95)>As(6.57)>Mn(5.22)>Zn(2.7)>Hg(2.48)>Ca(2.03)>Co(0.69)>Ni(0.09)>Mg(0.08)>Cr(0.03).

The contents of these 17 metals all wavily varied with depth without rules. The relative standard deviation of metals in every core indicated Ba, Hg and B varied greatest with average values of 60.7% (41.3%–93.4%), 52.6% (19.0%–117%) and 45.5% (26.6%–55.9%), respectively. Besides, Pb also varied greatly in Stations 2, 3, 4 and 7 with the relative standard deviation of 95.9%, 78.2%, 43.7% and 40.7% respectively due to high contents in some depths.

3.2 Baseline value establishment

In this paper, any metal content deviating away from its average value by ± 5 standard deviations was removed from the data set to define the baseline value (Veinott et al., 2001). This screening process resulted in the identification of 7 anomalous points, including five data points for Ba and two data points for Hg, which were not calculated to define the baseline value.

The baseline values of the 17 evaluated metals were determined using the normalization method and the cumulative frequency curve method. The baseline values of the former were higher than those from the latter, which was caused by the elimination of values outside the 95% confidence interval of the linear regression equations in the standardization method. However, the baseline values obtained by the two methods agreed well with each other, excluding Pb. Therefore, the average baseline value was computed through the two methods as the final baseline value of metal in the research area (Table 2). The normalization and cumulative curves of metals are shown in Figs 3 and 4.

4 Discussion

4.1 Different inert elements in normalization method

The highest correlation coefficients between active metals and inert elements are marked in gray in Table 3. Inert elements are known to induce metallogenesis; therefore, 17 metals were dominated by natural geological metallogenic processes, which was minimally influenced by human activities. Nevertheless, the correlation coefficient between the 17 metals and inert elements varied for each metal, indicating slight differences in the influence of mineralization and the variable sources of 17 metals. This may also explain the discrepancies between the 17 metals in the cumulative frequency at the inflection point.

4.2 Different cumulative frequencies corresponding to an inflection point in the cumulative frequency curve method

Figure 4 shows that two inflection points occurred in the cumulative frequency curve of four elements, i.e., Cu, Cr, Pb, and Ag. At the higher inflection point, the cumulative frequency for these metals was above 80%; the samples exceeding the higher inflection point may be influenced by human activities, but the ratio is small. In addition, only one inflection point appeared in the cumulative curves of the other thirteen metals (Ba, Ca, K, Mg, Mn, Na, As, B, Cd, Co, Hg, Ni, and Zn); these metals were all an-

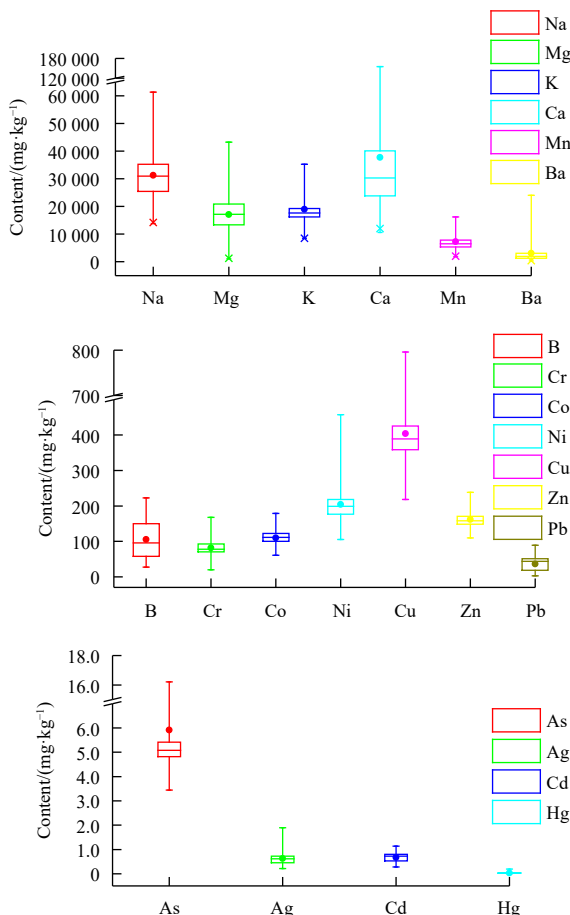


Fig. 2. Box chart of metal contents.

Table 2. Baseline value of metals through two methods

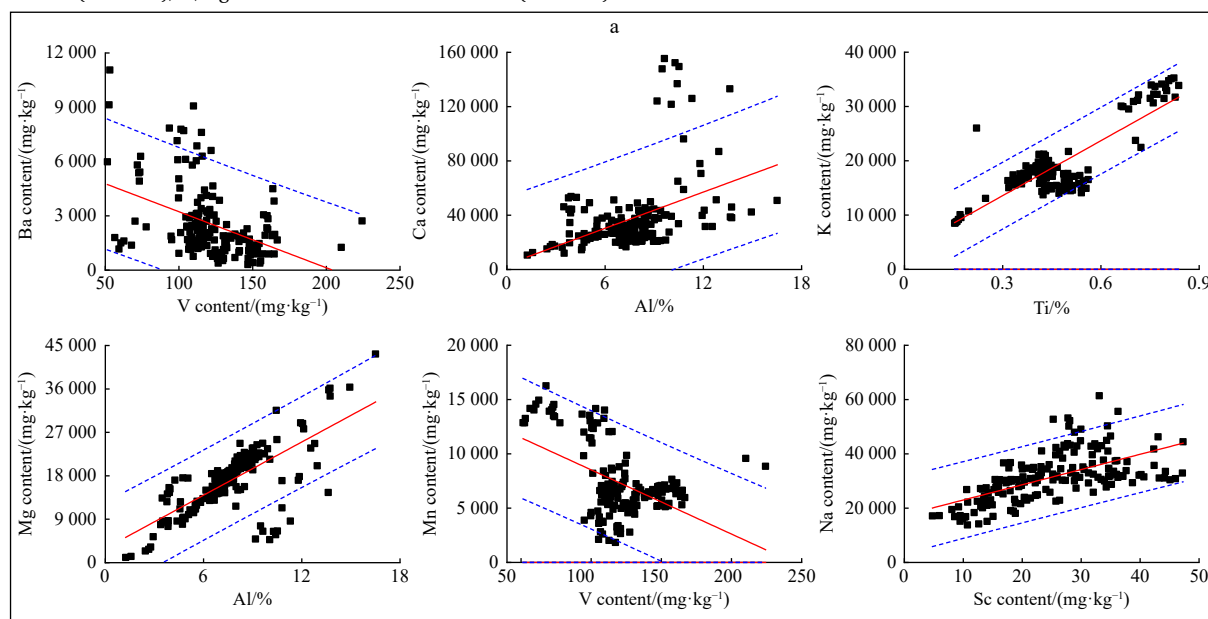
Metal	Normalization method		Cumulative curve method			Final baseline value	
	Regression equation	R^2	Baseline value/(mg·kg ⁻¹)	First inflection	Second inflection		Baseline value/(mg·kg ⁻¹)
Ba	Ba=-18.9·V+4 536	0.12	2 230	3 110	-	1 633	1 932
Ca	Ca=2 218.2·Al+15 555.2	0.19	32 214	43 950	-	26 810	29 512
K	K=35 394.5·Ti+2 729.9	0.77	19 047	19 500	-	17 253	18 150
Mg	Mg=2 270.4·Al+618.3	0.80	17 624	24 690	-	16 615	17 120
Mn	Mn=-69.1·V+15 436.2	0.31	7 144	12 860	-	6 350	6 747
Na	Na=512.1·Sc+17 681.4	0.43	30 228	31 920	-	26 864	28 546
Ag	Ag=0.012 9·Sc+0.279	0.34	0.598	0.671	0.928	0.543	0.571
As	As=0.013 3·V+3.43	0.49	5.01	5.42	-	4.98	5.00
B	B=-2.32·Li+205	0.39	105	173.1	-	83.8	94.4
Cd	Cd=0.015·Sc+0.283	0.63	0.663	0.783	-	0.588	0.626
Co	Co=0.606·V+36.9	0.82	110	110	-	97.9	104
Cr	Cr=0.906·V-27.6	0.93	82.0	76.7	118	70.1	76.1
Cu	Cu=3.21·Li+259	0.39	393	378	462	347	370
Hg	Hg=0.002 89·Cs+0.013 1	0.19	0.031	0.079	-	0.025	0.028
Ni	Ni=-19.4·Fe+286	0.31	194	216	-	186	190
Pb	Pb=0.412·V-11.8	0.42	37.6	43.0	52.7	17.4	27.5
Zn	Zn=0.855·Li+123	0.33	160	167	-	152	156

Note: Metal symbol in regression equation represents the content of corresponding metal; - represents no data.

Table 3. Correlation coefficient of 17 metals

	Al	Ti	Fe	Li	V	Rb	Sc	Cs	La
Ba	0.310**	0.275**	0.407**	-0.228**	-0.426**	-0.275**	0.152*	-0.194*	0.253**
Ca	0.519**	0.517**	0.394**	-0.355**	-0.298**	-0.137	0.260**	-0.378**	0.347**
K	0.738**	0.838**	0.789**	-0.424**	-0.179*	-0.161*	0.317**	-0.171*	0.548**
Mg	0.786**	0.110	0.245**	0.417**	-0.027	0.298**	0.255**	0.129	0.770**
Mn	0.303**	0.365**	0.236**	-0.194*	-0.503**	-0.329**	0.128	-0.421**	0.303**
Na	0.050	-0.092	0.141	0.080	-0.531**	0.170*	0.611**	0.426**	0.292**
Ag	0.000	0.049	0.167*	-0.091	-0.493**	-0.163*	0.519**	0.310**	0.113
As	-0.010	-0.140	0.275**	0.113	0.310**	0.281**	0.033	0.133	0.034
B	-0.444**	-0.109	-0.083	-0.480**	-0.086	-0.151*	-0.156*	-0.024	-0.477**
Cd	0.099	0.288**	0.410**	-0.211**	-0.282**	0.031	0.720**	0.210**	0.272**
Co	0.007	0.053	-0.177*	0.267**	0.848**	0.162*	-0.240**	-0.139	-0.194*
Cr	0.111	0.365**	0.065	-0.065	0.964**	0.083	-0.351**	-0.231**	-0.205*
Cu	-0.343**	-0.618**	-0.399**	0.626**	-0.174*	0.101	0.172*	0.086	-0.009
Hg	-0.050	-0.143	0.255**	-0.019	-0.222**	0.222**	0.325**	0.433**	0.154
Ni	-0.332**	-0.395**	-0.525**	0.394**	-0.135	-0.047	-0.079	-0.185*	-0.187*
Pb	-0.053	0.142	-0.052	-0.237**	0.584**	-0.018	-0.528**	-0.170*	-0.315**
Zn	-0.069	-0.230**	-0.226**	0.395**	-0.061	0.171*	0.084	-0.166*	0.042

Note: The highest correlation coefficients between active metals and inert elements are marked in gray. * represents significant correlation at 0.05 level (two tails); **, significant correlation at 0.01 level (two tails).



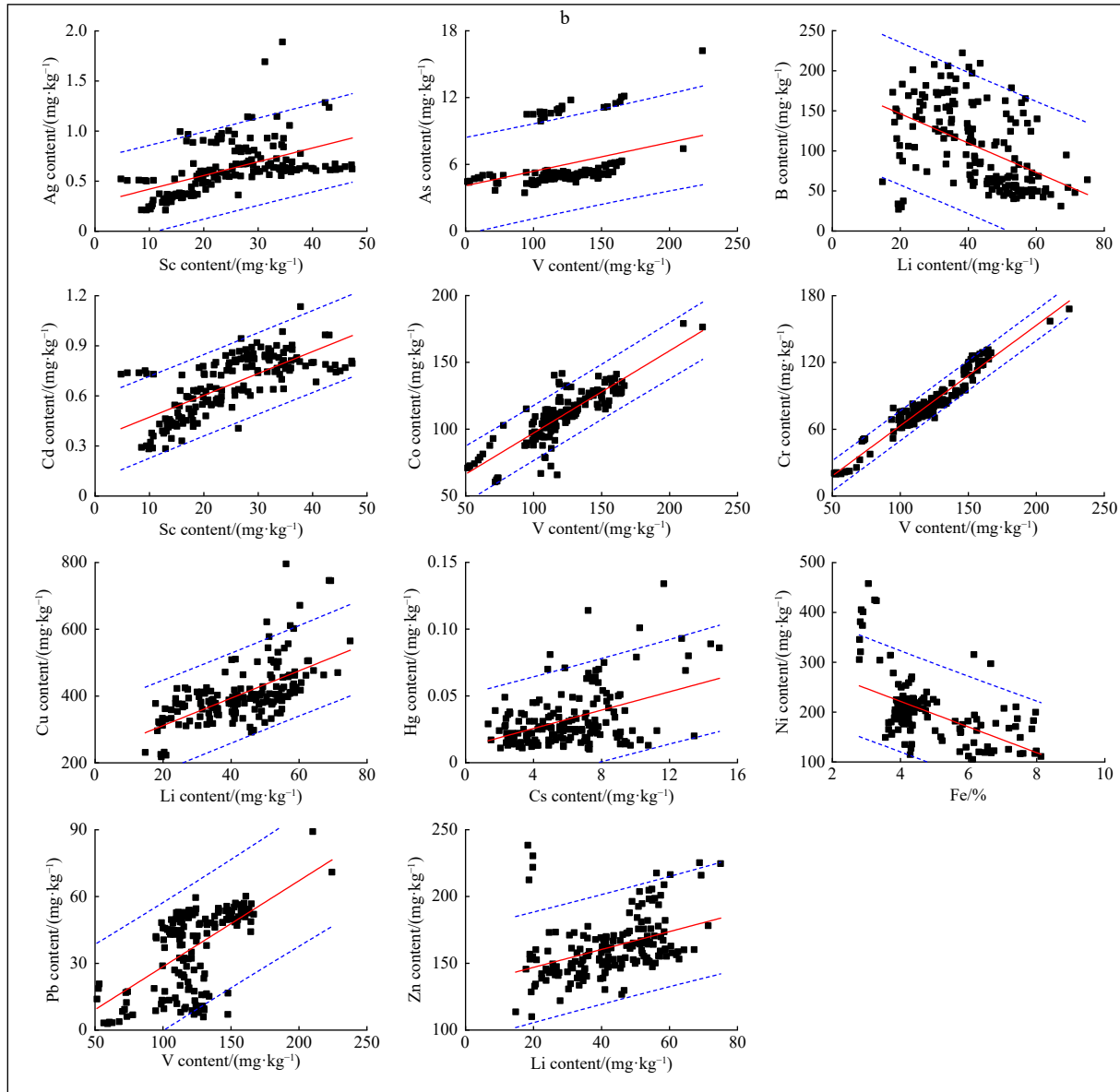


Fig. 3. Normalization of the 17 evaluated metals. a. Major metals; b. trace metals.

thropogenically effected to a lesser extent (Li, 2013). Hence, the 17 metals in the study area were not substantially impacted by human activities.

According to Bischoff et al. (1979), $\frac{\omega(\text{TiO}_2)}{\omega(\text{Al}_2\text{O}_3)}$ and $\frac{\omega(\text{Fe}_2\text{O}_3)}{\omega(\text{Al}_2\text{O}_3)}$ could be used to indicate the sediment sources due to the dilution effect of Al relative to other elements. $\frac{\omega(\text{TiO}_2)}{\omega(\text{Al}_2\text{O}_3)} = 0.05$ and $\frac{\omega(\text{Fe}_2\text{O}_3)}{\omega(\text{Al}_2\text{O}_3)} = 0.46$, $\frac{\omega(\text{TiO}_2)}{\omega(\text{Al}_2\text{O}_3)} = 0.09$ and $\frac{\omega(\text{Fe}_2\text{O}_3)}{\omega(\text{Al}_2\text{O}_3)} = 0.55$, and $\frac{\omega(\text{TiO}_2)}{\omega(\text{Al}_2\text{O}_3)} = 0.11$ and $\frac{\omega(\text{Fe}_2\text{O}_3)}{\omega(\text{Al}_2\text{O}_3)} = 1.18$ represent pelagic clay sources, volcanic activities and biological activities, respectively. In this study, $\frac{\omega(\text{TiO}_2)}{\omega(\text{Al}_2\text{O}_3)} = 0.02 - 0.36$, with a mean value of 0.06, while $\frac{\omega(\text{Fe}_2\text{O}_3)}{\omega(\text{Al}_2\text{O}_3)} = 0.22 - 2.42$ had an average value of 0.51. However, if we excluded the sample at Station 8 collected in the range of 34-cm depth to the bottom, the above ratios ranged from 0.02 to 0.09, with an average value of 0.05, and from 0.22 to 1.13, with an

average of 0.48. This result indicated that the sediment in the research area originated mainly from pelagic clay sources followed by volcanic activities. At Station 8, within the 34-cm depth to bottom interval, the above ratios ranged from 0.15 to 0.36, with an average value of 0.23; and from 1.07 to 2.42, with an average value of 1.53. This result indicated that these sediments were dominated by biological activities. Therefore, anthropogenic activities played a minor role in the distribution of the 17 metals, which was in good agreement with the inflection points in the cumulative curves.

4.3 Differences in the baseline values from two methods

As shown in Table 4, the relative deviation between the average value and median value for the 17 metals was in the order of Ba>Hg>Ca>Pb>As>Mn>B>Cd>K>Cr>Cu>Ni>Zn>Ag>Mg>Na>Co. Additionally, for the four metals (Ba, Ca, Hg, and Pb), the relative deviation of the baseline values from the two methods was also ranked first. This was because with the higher relative deviation between the average value and the median value, the contents of

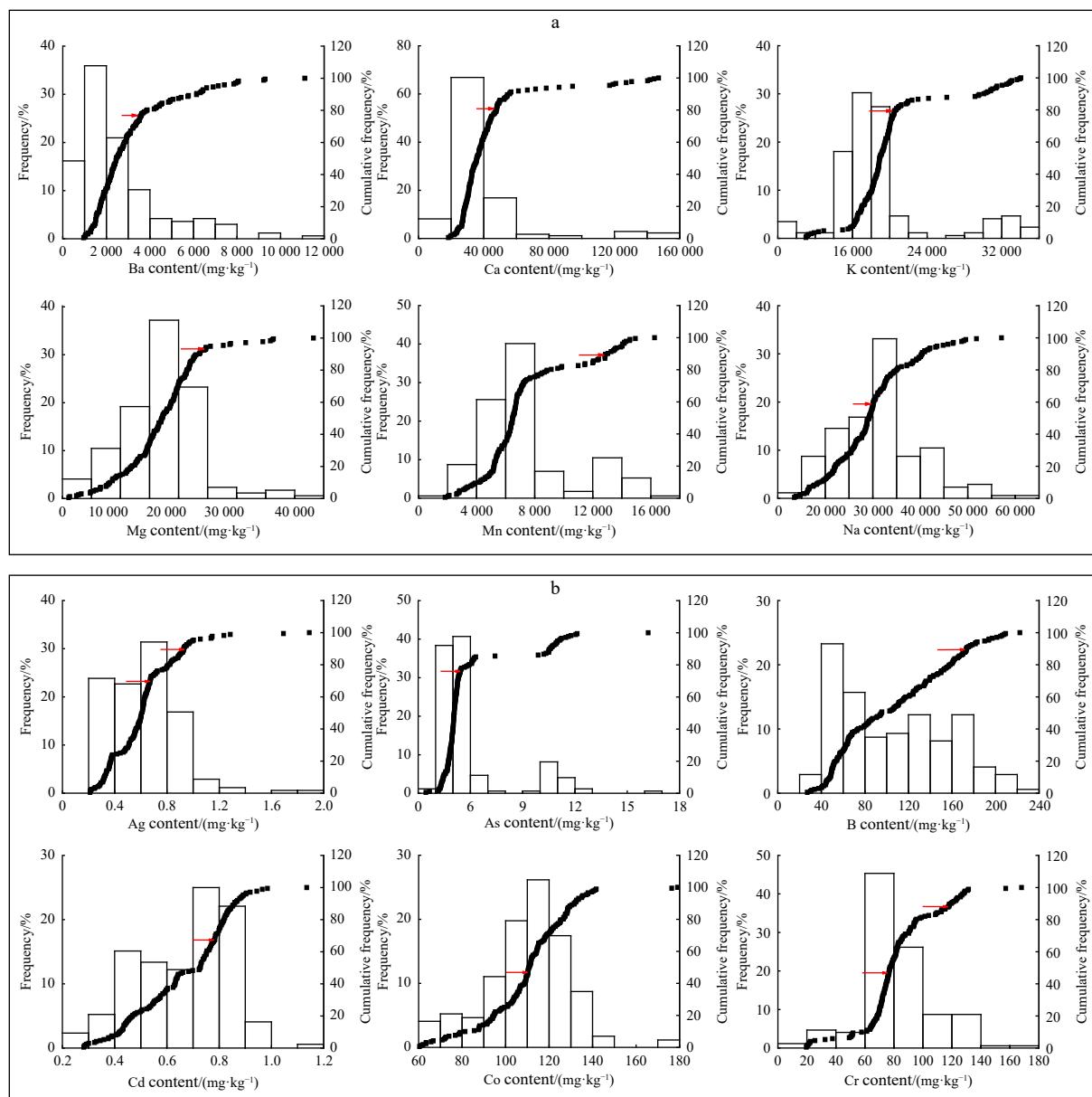
metals were better characterized by a partial distribution pattern, which introduced error into the cumulative frequency curve method.

The relative deviation of the baseline values for metals obtained from the two methods was less than 16%, excluding Pb. Pb contents ranged mostly from 5.0 mg/kg to 25.0 mg/kg and from 40.0 mg/kg to 60.0 mg/kg, so for those samples with Pb concentrations lower than 42.6 mg/kg, which represented the lower inflection point in the cumulative frequency curve, the median Pb content was only 17.4 mg/kg. However, the baseline value of Pb derived through the standardization method was 37.6 mg/kg. The relative deviation of the Pb baseline value through the two methods reached 36.7%. Wei and Wen (2012) reported the baseline value of Cr in the Taihu Lake employing normalization and the cumulative frequency curve method, as 123.75 mg/kg and 77.37 mg/kg, respectively, with a relative deviation of 23.0%. They also obtained the baseline value of Zn in the Dianchi Lake from the two methods, which were 263.56 mg/kg and 153.95 mg/kg, respectively, with a relative deviation of 26.3%. Hence, the

results of the two methods are considered reasonable for all 17 metals, including Pb.

4.4 Comparison of baseline values considering average and median values

Figure 5 indicates no obvious difference between the baseline value and the average value or median value for the 17 metals. The average relative deviation of the baseline value and average value or the baseline value and median value for the 17 metals were 6.4% (0.3%–23.3%) and 3.4% (0.3%–22.6%), respectively, and both could be considered parallel samples for trace metals according to General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China, Standardization Administration of China (2008). As described in Section 2.3.2, when the accumulative frequency curve was near linear, the baseline value was calculated using all samples; the baseline value was almost equal to the average or median value, so the metals in the study area were again considered less affected by human activities and the two methods were feasible.



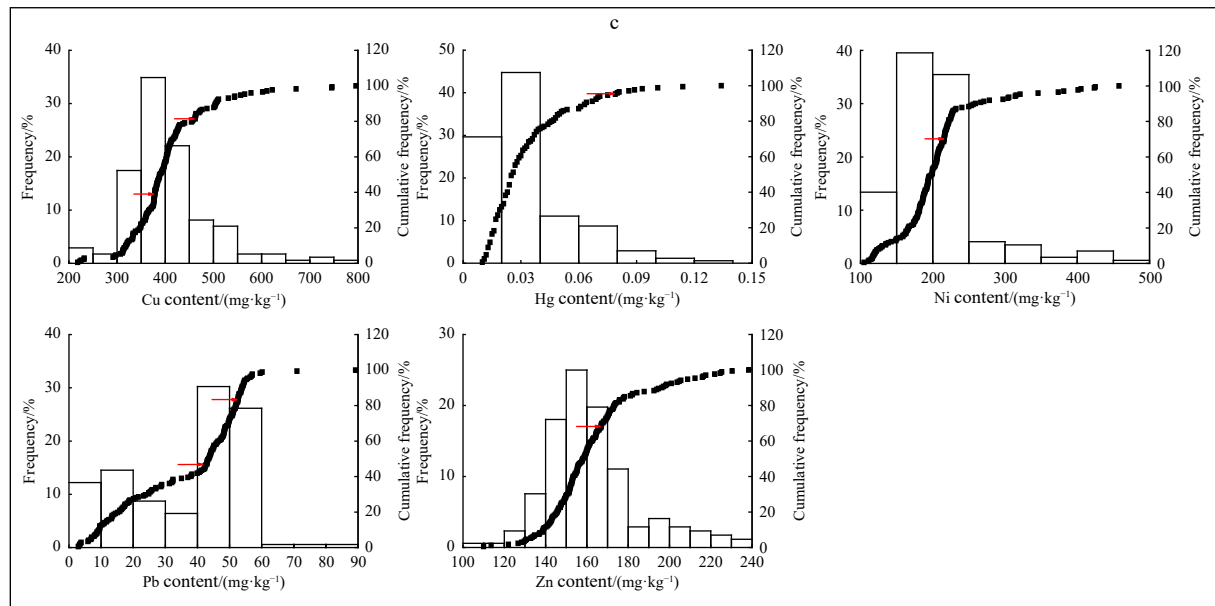


Fig. 4. Cumulative frequency curves of the 17 evaluated metals. a. Major metals; b and c. trace metals.

Table 4. Relative deviation of average value and median value and that of baseline values obtained by two methods

Metal	Relative deviation of average value and median value/%	Relative deviation of baseline value obtained by two methods/%
Ba	21.9	15.5
Hg	14.8	10.7
Ca	11.0	9.3
Pb	8.8	36.7
As	7.6	0.3
Mn	5.9	5.6
B	4.7	11.2
Cd	4.2	6.0
K	3.6	4.7
Cr	2.7	7.8
Cu	1.8	6.2
Ni	1.2	2.1
Zn	1.2	2.6
Ag	0.7	4.8
Mg	0.6	2.9
Na	0.5	5.8
Co	0.4	5.8

4.5 Comparison of baseline values with other baseline values

A comparison between the baseline values of metal concentrations in the western CCZ and those in other areas in the world is shown in Table 5. The baseline values of Mn, Co, Cu, and Ni were all higher than those reported for oceanic sediments, Pacific pelagic clays, and coastal sediments, which was consistent with the high contents of metals caused by full polymetallic nodules in the study area. The Dianchi Lake is surrounded by mountains consisting of bedrock of limestone and shale, and contains pollutants discharged from rural industries, predominantly the chemical, textile, building material, metal processing, electroplate, engineering and electronic industries, so the high baseline values of As, Hg, Cr, Pb and Zn are caused by large anthropogenic inputs and high geochemical background concentrations (Wei and Wen, 2013). Hence, the baseline values of the above five metals were 0.5 to 8 times higher than those in the study area. The Taihu Lake was also influenced by industrialization and urbanization but to a lesser extent than the Dianchi Lake, so the

baseline values of As, Hg, Cr and Pb were approximately 50% of those in the Dianchi Lake but higher than those in the study area, especially that of Hg, which exhibited a 4-fold increase. Therefore, the variation in the baseline values of metals in different areas could be attributed to the combined effects of the geological sedimentary environment and human activities. On the other hand, it also indicated that the baseline values obtained through the two methods in this paper were reliable.

5 Conclusions

Normalization and the cumulative frequency curve method were both employed to obtain the baseline values for certain metals. In the western CCZ, the baseline values of 17 metals (Ba, Ca, K, Mg, Mn, Na, Ag, As, B, Cd, Co, Cr, Cu, Hg, Ni, Pb, and Zn) were established with the values of 1 932 mg/kg, 29 512 mg/kg, 18 150 mg/kg, 17 120 mg/kg, 6 747 mg/kg, 28 546 mg/kg, 0.571 mg/kg, 5.00 mg/kg, 94.4 mg/kg, 0.626 mg/kg, 104 mg/kg, 76.1 mg/kg, 370 mg/kg, 0.028 mg/kg, 190 mg/kg, 27.5 mg/kg and 156 mg/kg, re-

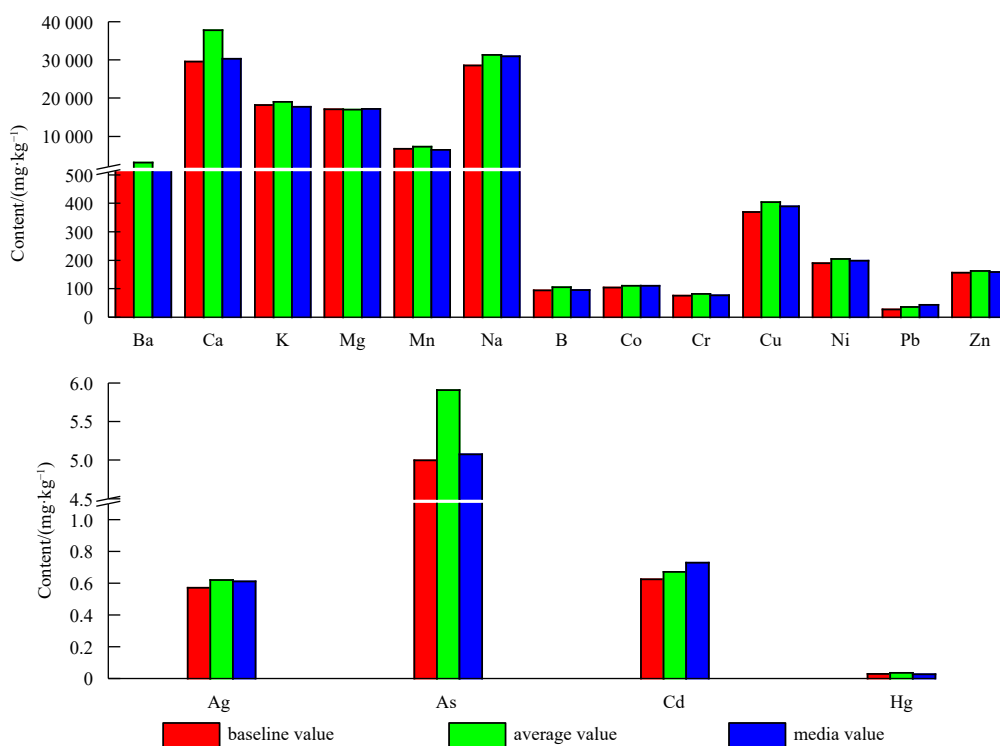


Fig. 5. Comparison of baseline value with average and median values.

Table 5. Comparison of baseline values ($\text{mg}\cdot\text{kg}^{-1}$) in different areas

	Ba	Ca	K	Mg	Mn	Na	Ag	As	B	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn
Baseline value in this paper	1 932	29 512	18 150	17 120	6 747	28 546	0.571	5.00	94.4	0.626	104	76.1	370	0.028	190	27.5	156
Average value in oceanic sediment (Lv, 2005)	-	4 286	17 426	13 080	3 176	8 161	-	-	-	-	-	-	-	-	-	-	-
Average value in Pacific pelagic clay (Bischoff et al., 1979)	3 900	5 000	22 404	20 400	4 338	9 645	-	-	-	-	74	90	230	-	225	-	965
Baseline value of the Liao River watershed sediment (Jiang et al., 2013)	-	-	-	-	-	-	-	-	-	-	-	60	21	-	27	23	96
Baseline value of the Tuohu River (Li, 2013)	-	-	-	-	604.84	-	-	20.58	-	-	-	74.73	25.14	-	20.65	22.43	72.17
Baseline value in the Taihu Lake (Wei and Wen, 2012)	-	-	-	-	-	-	-	9.92	-	-	22.62	100.56	31.63	0.14	31.97	33.05	97.01
Baseline value in the Dianchi Lake (Wei and Wen, 2012)	-	-	-	-	-	-	-	24.60	-	-	36.78	135.68	90.05	0.25	50.76	73.56	208.76
Baseline value of the Ganges River (Singh et al., 2003)	-	-	-	-	1 764	-	-	-	-	0.58	19.2	147	55	-	47	22	105
Baseline value of the Baleh River (Sim, 2016)	-	-	-	-	823	-	-	-	-	-	-	73.90	38.07	0.34	32.70	31.35	73.15

Note: - represents no data.

spectively. It would provide basic data support for the research of environmental baseline and may help to improve the accuracy of environment impact assessment of mining exploitation.

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