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FRACTIONATION AND ENVIRONMENTAL RISK OF TRACE METALS IN SURFACE SEDIMENT OF THE EAST CHINA SEA BY MODIFIED BCR SEQUENTIAL EXTRACTION METHOD

FRAKSINASI DAN RESIKO LINGKUNGAN DARI *TRACE METALS* PADA SEDIMEN PERMUKAAN LAUT TIMUR CINA MENGGUNAKAN MODIFIKASI METODE EKSTRAKSI SEKUENSIAL *BCR*

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ABSTRACT

Geochemical fractionation of Cadmium (Cd), Lead (Pb), Cobalt (Co), Zink (Zn), Iron (Fe) and Manganese (Mn) in sediment of the East China Sea were determined using four-stages of modified BCR sequential extraction method combination with ICP-MS. The total concentration of trace metals in sediment samples were in the following order: Fe >Mn>Pb> Zn > Co > Cd. Cd is present mainly in acid soluble fraction. Pb and Mn are in the group with presenting of easy reducible fraction and acid soluble fraction. Fe and Co were found in a group with mainly in residual fraction, while Zn was distributed in all four fractions. The highest contamination factors were found for Cd and Mn while the lowest were found for Fe and Co in almost station. The result showed low risk for Fe and Co in all station, Pb (except S2 and S3), Zn at S3,S6 and S7, and Mn at S1. A medium risk is indicated for Pb at S2 and S3, Zn at S1 and S5, and Mn at S2 and S6. A high risk showed for Zn at S2 and S4, and Mn at S4 and S5, while Cd at almost station (except S4) was very high risk.

Keywords : BCR sequential extraction, contamination factor, East China Sea, trace metals

ABSTRAK

Fraksinasi geokimia dari Cadmium (Cd), Timbal (Pb), Cobalt (Co), Zink (Zn), besi (Fe) dan Mangan (Mn) pada sedimen permukaan Laut Cina Timur di 7 stasiun (S) ditentukan dengan menggunakan empat tahapan metode ekstraksi sekuensial BCR kombinasi dengan ICP-MS. Konsentrasi total *trace metals* dalam sampel sedimen berada di urutan sebagai berikut: Fe> Mn> Pb> Zn> Co> Cd. Cd hadir terutama dalam fraksi larut dalam asam. Pb dan Mn berada dalam kelompok dengan menghadirkan fraksi yang mudah direduksi dan fraksi larut dalam asam. Fe dan Co ditemukan dalam kelompok fraksi residu, sementara Zn didistribusikan dalam semua fraksi. Faktor kontaminasi tertinggi ditemukan untuk Cd dan Mn sedangkan terendah ditemukan untuk Fe dan Co di hampir semua stasiun. Hasil penelitian menunjukkan risiko rendah untuk Fe dan Co dalam semua stasiun, Pb (kecuali S2 dan S3), Zn di S3, S6 dan S7, dan Mn di S1. Risiko menengah diindikasikan untuk Pb di S2 dan S3, Zn di S1 dan S5, dan Mn di S2 dan S6. Resiko tinggi terindikasi untuk Zn di S2 dan S4, dan Mn pada S4 dan S5, sementara Cd di hampir semua stasiun (kecuali S4) terindikasi risiko yang sangat tinggi.

Kata Kunci: ekstraksi sekuensial BCR, faktor kontaminasi, Laut Timur Cina, *trace metals*

INTRODUCTION

Metal and metalloid can accumulated in sediment, sludge and soil may therefore pose an environmental problem concerning possible metal transfer from sediment to the aquatic system and including them in the food chain (Wuana & Okiemen, 2011). Furthermore, contaminant content of sediment also be significantly modified and regulated by reaction occurring on the surface of particles in the sediment (sorption/desorption), which also play a significant role in speciation and contaminant bioavailability (Gonzales, Thuovenin, Dange, Chiffoleau, & Boutier, 2006).

Heavy metals or trace metals are of particular concern owing to their environmental persistence, bio-geochemical, and toxicity risk (Dhanakumar, Rutharvel, Solaraj, & Mohanraj, 2013). Previous study of trace metals mainly focus on their total concentration in sediment (Fang, Li, Feng, & Chen, 2009; Feng, Huang, Zhang, Tian & Zeng, 2012; Miola, Morai, & Pinheiro, 2016). But this data is poor indicator of bioavailability, mobility or toxicity; these properties basically depend on the chemical bonding between metals and solid phases of the samples. Metal ions in sediments are partitioned between the different phases, i.e., organic matter, oxyhydroxides of iron, aluminum and manganese, phyllosilicate minerals, carbonates and sulfides. In addition, metal ions are retained in the solid phase by different mechanisms (ion exchange, outer and inner-sphere surface complexation (adsorption), precipitation or co-precipitation.

European Community Bureau of Reference (BCR) sequential methods commonly used to fractionated trace metals in the sediment or soil samples. This method can be provide information about the identification of the main binding site, the strength of metal binding to the particulates and the phase association of the trace metals in sediment. Some studies have been carried out and some good articles have already been published by using this method for various samples (Zemberyova, Bartekova, & Hagarova 2006; Baig et al. 2009; Nemati, Abu Bakar, Abas, & Sobhanzadeh, 2011).

The East China Sea (ECS) located between 26^{o}-32^{o} N and 121^{o} -128 ^{o} N, one of the largest marginal seas in the world, is an important terrestrial organic carbon sink. Large amounts of terrestrial particulate matters with organic matters are discharged into the ECS via the Changjiang River (CR). Some recent studies conducted on trace metals in surface sediment in ECS (Fang et al. 2009; Liu et al. 2011; Yu, Jinming, Xuegang, Huamao, & Ning, 2013; Xu, Liu, Pei, Hu, & Kong, 2015), located in inner shelf continent. Approximately 55–70% and 10–17% of the sedimentation fluxes of trace metals were deposited in the inner shelf and the Changjiang estuarine zone (Fang et al., 2009). However, the distribution and contamination status of trace metals for the outer shelf continent in ECS has not been studied. In order to establish such a knowledge, the present study investigates the spatial distribution of trace metals including mobility and the pattern of spread of trace metals in sediment of the outer shelf continent of ECS.

The main objective of this work was to compare the results obtained from using the modified BCR sequential extraction method at surface sediment in the ECS (outer shelf continent) and discuss the mobility potential of trace metals. The trace metal contents of Cadmium (Cd), Lead (Pb), Cobalt (Co), Zink (Zn), Iron (Fe) and Manganese (Mn) in the extracts were measured by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Also the contamination factors and risk assessment code effects on surface sediment samples are discussed.

EXPERIMENTAL

Materials and Tools

The materials used, among others: Sediment sample from 7 locations at the East China Sea, hydrochloric acid, acetic acid, hydrofluoric acid, hydroxyl ammonium chloride, hydrogen peroxide, ammonium acetate, and MilliQ (deionized water). Instruments used were ICP-MS (HP 4500, Japan), pH meter (TOA, HM-26S, Japan), and a polyethylene volumetric flask.

Sampling and Sample Pretreatment

The sediment samples from seven locations in the East China Sea (outer shelf continent) were selected on 24-28 September 2012 with the cruise name KT-12-25 (**Figure 1**), collected from the bottom of the sea by multi core sediment sampling. The top sediments (0-3 cm) was taken and sub sampled by plastic spatula then sealed in PTFE bags and storage at low temperature (-5 °C). The dry sample are easier to be treat than wet sample, so in our work, I used cold dryer that can dry the samples at -40 °C. Dry sample were used for the sequential extraction procedure analytical method. Inductively Coupled plasma-mass spectrometry (ICP-MS HP 4500, Japan) was applied to determination of traces metals in this work. A horizon shaker was used for the extraction and pH meter was used to measurement pH value of the extraction. An ultracentrifuge was used for centrifugation of the extract. All the teflon, glass and plastic containers used was cleaned by aqua regia (HCl : HNO_3 = 3:1) and rinse with MilliQ water (deionized water). The extract of the sample were stored in PTFE tubes and stored at 4 ^oC before analysis.

Pseudo Total Metal Digestion

Total concentration of trace metals in sediment were determined by digestion with mixture of aqua regia and HF. One gram of the sediment sample and 20 mL of mixture acid (15 mL HNO_3 + 5 mL HCl + 2 mL HF) were heated in sand-bath heater. Digests were filtered by Whatman filter paper into the 50 mL of volumetric flasks.

Sequential Extraction Methods

Sequential extraction was performed using three stage modified procedure recommended BCR plus the residual fraction (Nemati et al. 2011). All extraction was carry-out for 16 h (overnight) at room temperature using mechanical shaker. The extract separated by centrifugation for 25 minutes at 3000 rpm, and resultant supernatant liquid was transferred into a polyethylene volumetric flask. The residue was washed by adding 20 mL of deionized water, shaken for 15 minutes on the end-over-end shaker, and centrifuged for 20 minutes at 3000 rpm.

Step 1 (Acid extractable /exchangeable fraction): 40 mL of 0.11M acetic acid (Solution I) was added to 1 gram sediment sample in centrifuge tube and shaken for 16 h at room temperature. The extract was then separated from the solid residue by centrifugation and filtrate was separated by decantation as previously described

Step 2 (easy reducible fraction): 40 mL of a freshly prepared hydroxyl-ammonium chloride (solution II) was added to the residue from step 1 in the centrifuge tube, and re-suspended by mechanical shaking for 16 h at room temperature. The separation of the extract, collection of supernatant, and rinsing of residues were the same as describe in step 1.

Step 3 (Oxidizable fraction): the residue from step 2 was treated twice with 10 mL of 8.8 M hydrogen peroxide (solution III). First, 10 mL of hydrogen peroxide was added to the residue from step 2 in the centrifuge tube. The digestion was allowed to proceed at the room temperature for 1 h with occasional manual shaker, followed by digestion at 85 2 ^{o}C for another 1 h in a water bath. During the digestion, the centrifuge tube was loosely covered to prevent the substantial loss of hydrogen peroxide. Following that, the centrifuge tube was uncovered and heating was continued until the volume reduced to about 2-3 mL. An additional 10 mL of hydrogen peroxide was added to the tube, covered, and digested with cover at the volume reduced to 2-3 mL. Finally, 50 mL of 1.0 M ammonium acetate (solution IV) was added to the cold mixture and shaken for 16 h at room temperature. The separation of the extract, collection of supernatant, and rinsing of residues were the same described in step 1

Step 4 (residual fraction): The residue from step 3 was digested using a mixture of *aqua regia* ($HCl:HNO_3$ = 3:1) and HF.

RESULTS AND DISCUSSION

Reproducibility and Accuracy of BCR Sequential Extraction Method

To evaluate the reproducibility and accuracy of the method, a reference sediment material (GBW-07310) was subjected to BCR protocol. Three subsamples (set A, B, C) were taken through BCR sequential extraction method in parallel. The result and the relative standard deviation (RSD) are listed in **Table 1**. Result showed in **Table 1** indicated that method had a good reproducibility (and accuracy (RSD < 10%).

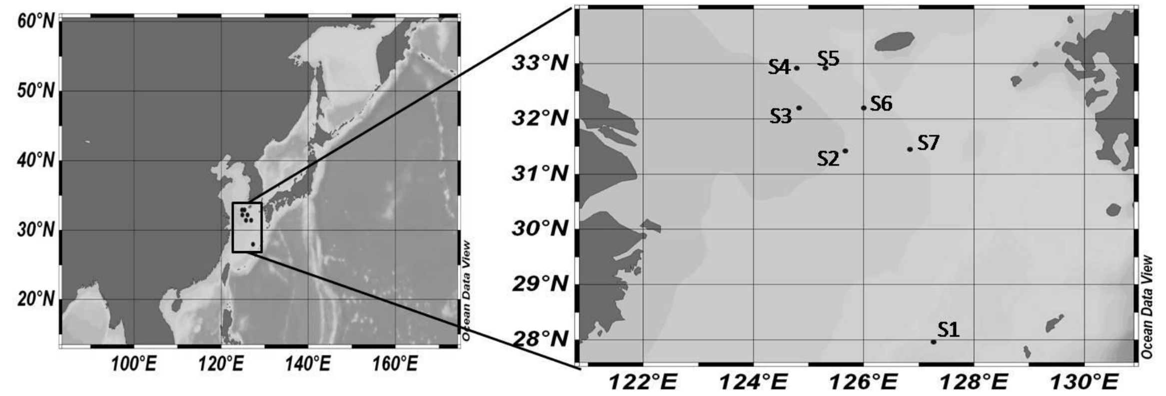

Figure 1. Sampling site

Table.1 Reproducibility of modified BCR sequential extraction method

Element	Fraction	Mean[a]	RSD[b]	Element	Fraction	Mean[a]	RSD[b]
Cd	Acid Soluble	0.22	3.07	Co	Acid Soluble	0.55	3.41
	Reducible	0.46	6.20		Reducible	7.43	2.12
	Oxidizable	0.12	6.71		Oxidizable	2.30	9.31
	Residual	0.18	4.61		Residual	2.49	1.32
Pb	Acid Soluble	0.02	7.81	Zn	Acid Soluble	4.46	6.31
	Reducible	10.22	5.52		Reducible	7.52	6.62
	Oxidizable	8.68	6.13		Oxidizable	11.90	5.73
	Residual	8.60	4.21		Residual	35.95	9.20
Mn	Acid Soluble	70.00	7.50				
	Reducible	416.04	3.72				
	Oxidizable	147.00	5.51				
	Residual	106.80	3.23				

[a]Units : µg.g^{-1}
[b]Units :%

Internal Check Recovery

An internal check was performed on the result of the sequential extraction by comparing the total amount of metals extracted by different reagents during the sequential extraction procedure with the result of the total digestion. The recovery was calculated as follow the equation:

$$Recovery = \frac{C_1 + C_2 + C_3 + C_4}{C_T} \ x \ 100\%$$

C_1 = C fraction 1
C_2 = C fraction 2
C_3 = C fraction 3
C_4 = C fraction 4
C_T = C total digestion

Result showed in **Table 2** indicated that the sum of the four fractions are in a good agreement with the total digestion and the methods used is reliable and repeatable.

Total Trace Metals Concentration

The result of pseudo total digestion of trace metals at sampling station (S) were presented in **Table 3**. The mean contents of the trace metals in surface sediment ECS were: Cd: 0.26; Pb: 32.38; Mn: 1059; Fe: 50898; Co: 13.17; and Zn: 27.96 μg.g^{-1}, allowing to arrange the trace metals concentration from higher to lower were in the following order: Fe >Mn>Pb>Zn>Co>Cd. The maximum concentrations were observed at the S2 and S3 which are nearest with the continental and decreasing trend to the farthest of the continental (**Figure 2**).

Table 2. Recovery of modified BCR sequential extraction method

Element	Concentration (μg.g^{-1})		Recovery
	Sum	Total digestion	(%)
Cd	0.66	0.67	97.92
Pb	41.68	44.71	93.22
Mn	1365.39	1390.44	98.19
Fe	37169.79	35268.54	105.39
Co	10.03	10.80	92.87
Zn	29.47	28.88	102.04

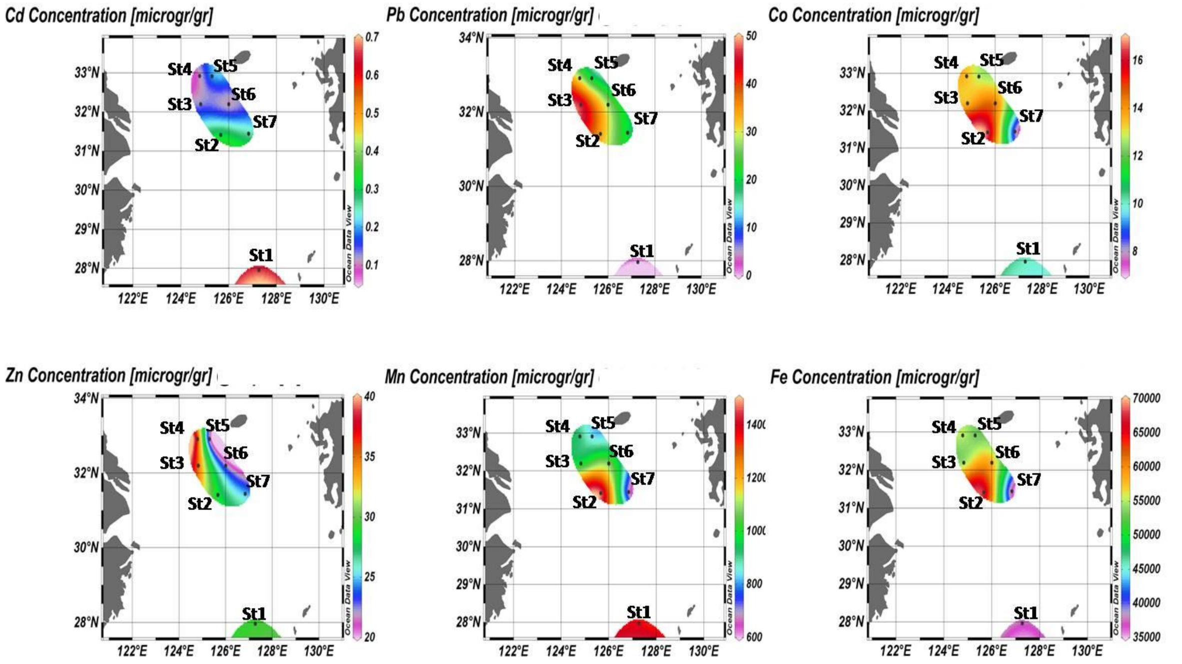

Figure 2. Distribution of total concentration of trace metals

Sequential Extraction Result

The trace metals concentration in the surface sediment sample from each step of extraction methods are shown in **Table 3.** The fractionation of trace metals in the surface sediment of the East China Sea (outer shelf continent) are divided into four groups depending on the degree of their association with the different phases. Cadmium (Cd) is present mainly in acid soluble fraction (more than 78% of the total concentration). Lead (Pb) and Manganese (Mn) are in the group with presenting of easy reducible fraction and acid soluble fraction. Iron (Fe) and Cobalt (Co) were found in a group with mainly in residual fraction (more than 75% of total concentration except Co at S1), while Zink (Zn) was distributed in all four fraction.

Cadmium

The levels of Cd in sediments or sludge were much concern for a long time because of its high toxicity. Several sequential extraction procedures, including the BCR protocol have been used to obtain information on the distribution of Cd in sediment (Naji, Ismail, & Ismail, 2010; Ahmadipour, Bahramifar, & Ghasempouri, 2014). In this study, Cd was also detected in the marine sediment following the BCR sequential extraction.

The dominant proportion of Cd (more than 78% except S4) was found in the acid soluble fraction, which indicated that most of Cd in the surface sediment is exchangeable. The trace metals in this fraction are adsorbed on sediments on their essential components namely clay, Fe and Mn hydrated oxides, and humic acids (Yuan et al, 2004). Weakly adsorbed Cd on the surface sediment by relatively weak electrostatic interaction maybe released by ion-exchange processes and dissociation of Cd-carbonate phase (Tersier, Campbell, & Bisson, 1979). The Cadmium in this fraction is the most labile, hence and easy to take up from sediment by the biota. This pattern was different with the result reported by Yuan C et al. (2004) and Yu et al. (2013) (inner shelf continent of ECS), who found that Cd mostly retained in the residual fraction.

Lead and Manganese

The distribution pattern of these two trace metals are illustrated in **Figure 3**. Pb and Mn were distributed in all fraction, but the dominant was in the easy reducible fraction. Pb and Mn showed variation between 25% and 79% in the reducible fraction while noticeable amount of Pb was observed in the acid soluble fraction (S2 and S3) and Mn at almost station except S2. The dominant in the reducible fraction mean that Pb and Mn exist as oxides and may be released if the sediment is subjected to more reduction condition. This fraction also indicated that Pb and Mn were labile and easy to take up from sediment. This pattern was different with the result reported by Yuan C et al. (2004) and Yu et al. (2013) (inner shelf continent of ECS), who found that Pb and Mn mainly retained in the residual fraction.

Iron and Cobalt

The pattern of distribution Fe and Co in the surface sediment of ECS mainly were found in the residual fraction. This pattern was similar with the result reported by Yuan et al. (2004), who found that Fe and Co mostly retained in the residual fraction. Trace metals associated with the residual fraction are likely to be incorporated in alumino-silicate minerals and unlikely released to pore water through dissociation. These elements are unlikely to pose direct and significant threaten to surrounding. Furthermore, Co at the station 1 showed the high concentration in the reducible fraction. In this case we have to make attention for this station.

Table 3. Concentration of trace metals by modified BCR sequential methods

	Cd (μg.$^{g1)}$	**Pb (μg.g^{-1})**	**Mn (μg.g^{-1})**	**Fe (μg.g^{-1})**	**Co (μg.g^{-1})**	**Zn (μg.g^{-1})**
Station No.1						
Acid Soluble	0.53	0.00	49.73	31.48	0.00	6.51
Reducible	0.11	27.88	1080.84	4039.36	4.52	12.70
Oxidizable	0.00	4.30	88.47	1249.56	0.11	2.40
Residual	0.02	9.49	146.35	31849.39	5.40	7.85
Pseudo -total	0.67	44.71	1390.44	35268.54	10.80	28.88
Cf	32.20	3.39	8.33	0.17	0.86	2.75
RAC (%)	80.06	0.00	3.64	0.08	0.00	22.10
Station No.2						
Acid Soluble	0.25	3.85	406.99	2668.78	0.00	11.67
Reducible	0.06	14.87	725.44	4081.08	2.14	4.00
Oxidizable	0.00	3.07	77.27	635.04	0.73	1.07
Residual	0.01	12.84	286.10	60624.71	14.01	11.69
Pseudo -total	0.33	35.62	1511.51	66766.70	17.11	27.77
Cf	31.28	1.70	4.23	0.12	0.21	1.43
RAC (%)	78.00	11.11	27.21	3.92	0.00	41.04
Station No.3						
Acid Soluble	0.12	12.18	388.20	545.42	0.00	1.66
Reducible	0.01	11.92	292.83	3551.54	1.59	10.21
Oxidizable	0.00	2.03	46.51	387.27	0.62	7.83
Residual	0.01	20.47	231.92	49215.77	11.12	15.53
Pseudo -total	0.15	45.88	980.01	53436.65	14.43	35.12
Cf	12.28	1.28	3.14	0.09	0.20	1.27
RAC (%)	87.40	26.14	40.46	1.02	0.00	4.72
Station No.4						
Acid Soluble	0.03	0.66	360.96	847.58	0.00	12.54
Reducible	0.05	13.64	300.13	3405.53	1.30	11.93
Oxidizable	0.00	5.50	60.66	4775.66	1.94	4.74
Residual	0.01	9.69	210.41	46438.10	10.39	8.86
Pseudo -total	0.11	30.11	940.55	55678.55	14.09	37.87
Cf	7.70	2.04	3.43	0.19	0.31	3.30
RAC (%)	36.15	2.24	38.72	1.53	0.00	32.94
Station No.5						
Acid Soluble	0.20	0.00	323.60	1384.78	0.00	4.98
Reducible	0.00	10.16	244.73	2979.56	1.07	3.13
Oxidizable	0.00	2.49	41.13	728.24	0.57	8.03
Residual	0.01	7.48	215.55	47829.21	10.96	4.49
Pseudo -total	0.20	21.11	830.97	51456.55	12.11	20.24
Cf	20.09	1.69	2.83	0.11	0.15	3.60
RAC (%)	95.26	0.01	39.22	2.62	0.00	24.15
Station No.6						

Acid Soluble	0.09	0.00	314.22	962.24	0.00	1.47
Reducible	0.00	15.02	466.48	3124.71	1.59	2.44
Oxidizable	0.00	2.86	58.04	724.60	0.62	13.20
Residual	0.01	10.00	251.16	53736.08	12.29	5.41
Pseudo -total	0.11	27.21	1077.65	57548.66	15.65	21.87
Cf	8.59	1.79	3.34	0.09	0.18	3.16
RAC (%)	89.57	0.00	28.83	1.64	0.00	6.54
Station No.7						
Acid Soluble	0.25	0.00	327.18	117.47	0.00	2.27
Reducible	0.00	8.73	164.72	2511.59	0.66	7.06
Oxidizable	0.00	2.69	31.44	1036.25	0.44	4.34
Residual	0.01	8.59	143.65	32524.17	6.90	11.20
Pseudo -total	0.27	22.01	687.21	36135.44	8.01	23.97
Cf	25.38	1.33	3.64	0.11	0.16	1.22
RAC (%)	96.21	0.00	49.05	0.32	0.00	9.11

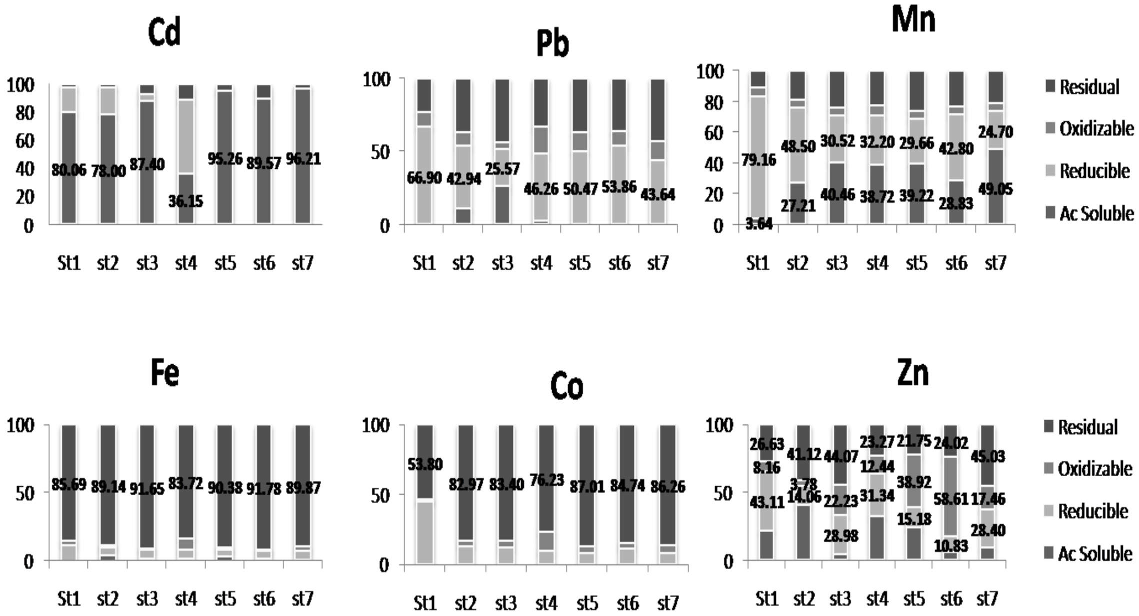

Figure 3. The average percentage of element speciation in difference stations

Zink

The distribution pattern of Zn was illustrated in **Figure 3**. Zn was distributed in all fractions, although the S1 mainly in reducible fraction, S2, S3 and S7 mainly in residual fraction, and S5 and S6 were mainly in oxidizable fraction. This pattern was different with the result reported by Yuan et al. (2004) and Yu et al. (2013) (inner shelf continent of ECS), who found that Zn mostly retained in the residual fraction.

Contamination Factor (Cf)

To know degree of trace metals risk to the environment in relation with its retention time, we need to calculate contaminant factor. A high contamination factor of trace metals shows low retention time and high risk to the environment. The individual contamination factor (Cf) was used to estimate the relative retention time of trace metals retained in the sediment. Its determined by dividing of the sum of each trace metal concentration in the mobile fraction (acid soluble, easy reducible and oxidizable) by its concentration in the residual fraction. Contamination factor of the each trace metals in the surface sediment in all station were shown in the **Figure 4**. Cd and Mn have a high contamination factor, that's mean the mobility of both trace metals were high and high risk to the environment. We have to make a serious attention for these elements. While another trace metals were not high risk to the environment, especially Pb and Zn have the lowest value of Cf.

Risk Assessment Code (RAC)

The risk assessment code (RAC), defined as the fraction of metal exchangeable and/or associated with carbonates (% F1 for BCR), was determinate for the six traces metals, and the value interpreted in accordance with the RAC classification described by Jain & Ran (2004). The RAC was determined base on the percentage of the total trace metal content that was found in the first sediment fraction in BCR method (% acid soluble fraction). This indicated trace metal are weakly bound to the solid phase. This condition means that the trace metal pose greater risk to the aquatic environment due to their greater potential (Jain et al., 2004). When this percentage mobility less than 1% ,the sediment has no risk to aquatic environment. Percentage of 1-10% reflects low risk, 11-30% medium risk, and 31-50% high risk. Above 50%, the sediment poses a very high risk and in considered dangerous, with metals easily able to enter the food chain (Jain et al. 2004).

In General, the data on **Table 4** shown low risk for Fe and Co in all station, Pb (except S2 and S3), Zn at S3,S6 and S7, and Mn at S1 with RAC less than 10%., so, there is not any significant trace metals mobility for these elements. A medium risk is indicated for Pb at S2 and S3, Zn at S1 and S5, and Mn at S2 and S6 that it can be noticeable in the early future. Zn at S2 and S4, and Mn at S4 and S5 show high risk, while Cd at almost station (except S4) was very high risk because very easy able to enter the food change.

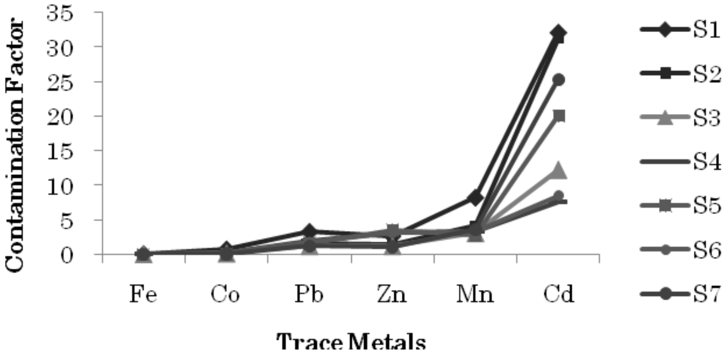

Figure 4. Estimated contamination factor of each trace metals

Table 4. Comparison of RAC values for all stations and elements

	Fe (%)	Co (%)	Pb (%)	Zn (%)	Mn (%)	Cd (%)
S1	0.08 (L)	0.00 (L)	0.00 (L)	22.10 (M)	3.64 (L)	80.06 (VH)
S2	3.92 (L)	0.00 (L)	11.11 (M)	41.04 (H)	27.21 (M)	78.00 (VH)
S3	1.02 (L)	0.00 (L)	26.14 (M)	4.27 (L)	40.46 (H)	87.40 (VH)
S4	1.53 (L)	0.00 (L)	2.24 (L)	32.94 (H)	38.72 (H)	36.15 (H)
S5	2.62 (L)	0.00 (L)	0.01 (L)	24.15 (M)	39.32 (H)	95.26 (VH)
S6	1.64 (L)	0.00 (L)	0.00 (L)	6.54 (L)	28.83 (M)	89.57 (VH)
S7	0.32 (L)	0.00 (L)	0.00 (L)	9.11 (L)	49.05 (H)	96.21 (VH)

L: Low; M: Medium; H: High, VH: Very High

CONCLUSION

The dominant proportion of Cd was found in the acid soluble fraction, which indicated that most of Cd is exchangeable, most labile, hence and easy to take up from sediment by the biota. Pb and Mn almost in the reducible fraction indicated that Pb and Mn were labile and easy to take up from sediment. Fe and Co in the surface sediment mainly were found in the residual fractions. Zn was distributed in all four fractions. The calculated contamination factor (Cf) showed that the highest Cf was obtained for Cd and Mn, then Pb and Zn while the lowest were found for Fe and Co.

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