



## Speciation of heavy metals by modified BCR sequential extraction procedure in different depths of sediments from Sungai Buloh, Selangor, Malaysia

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### ABSTRACT

The sequential extraction procedure proposed by the European Standard, Measurements and Testing (SM&T) program, formerly the Community Bureau of Reference (BCR), was applied for partitioning of heavy metals (HMs) in river sediments collected along the course of Sungai Buloh and the Straits of Malacca in Selangor, Malaysia. Eight elements (V, Pb, Cd, Cr, Co, Ni, Cu and Zn) from seven stations (S1–S7) and at different depths were analyzed using the modified BCR Sequential Extraction Procedure (SEP) in combination with ICP-MS to obtain the metal distribution patterns in this region. The results showed that heavy metal contaminations at S2 and S3 was more severe than at other sampling sites, especially for Zn, Cu, Ni and Pb. Nevertheless, the element concentrations from top to bottom layers decreased predominantly. The samples from the Straits of Malacca (S4–S7) the highest contamination factors obtained were for Co, Zn and Pb while the lowest were found for V and Cr, similar to Sungai Buloh sediments. The sediments showed a low risk for V, Cr, Cu and Pb with RAC values of less than 10%, but medium risk for Co, Zn (except S3), Cd at S1 and S2 and Ni at S1, S3 and S5. Zn at S3 and Cd at S3–S7 showed high risk to our sediment samples. There is not any element of very high risk conditions in the selected samples.

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### 1. Introduction

The contamination of sediments, soils, and biota by heavy metals (HMs) is of major concern, especially in many industrialized countries, because of their toxicity, persistence and bio-accumulative nature. Sediment samples have been found to be carriers of most metals and some elements may be recycled through biological and chemical reactions within the water column [1,2]. Metals and metalloids accumulated in sediments, sludge and soils may therefore pose an environmental problem concerning possible metal transfer from these samples to the aquatic medium, and thereby including them in the food chain [3]. The total metal content in polluted environmental samples is a poor indicator of bioavailability, mobility or toxicity; these properties basically depend on the different chemical forms of binding between trace metals and solid phases of the samples. Different metal extraction methods for environmental samples have been extensively studied [4]. Metal ions in sediments are partitioned between the different phases, i.e., organic matter, oxyhydroxides of iron, aluminum and manganese, phyllosilicate minerals, carbonates and sulphides. In addition, metal ions are retained in these solid phases by differ-

ent mechanisms (ion exchange, outer- and inner-sphere surface complexation (adsorption), precipitation or co-precipitation) [5]. Although the separation of various chemical forms of heavy metals is very difficult, the use of sequential extraction method proves to be an important and effective approach.

Single leaching and combined sequential extraction schemes have been developed to estimate the relative phase associations of sedimentary metals in various aquatic environments [6]. The two most widely utilized protocols are the Kersten/Forstner procedure [7] and the Tessier procedure [8]. However, as these procedures differ in extraction sequences and in operating conditions, it is quite difficult to compare the data obtained from these two methods.

In addition, the lack of suitable reference materials does not allow a comparison of results obtained independently by different laboratories using the adopted analytical protocol. Therefore, the European Community Bureau of Reference (BCR) has introduced a new, three-step sequential extraction and a modification of the method [9]. Some good articles have already been published with regard to the BCR method for various samples [10–15].

Sungai Buloh is a town in the state of Selangor, Malaysia. It is a 15-min drive from Sungai Buloh to Kuala Lumpur, the capital city of Malaysia. The name itself literally means “Bamboo River” in the Malay language. All the rivers in Kuala Lumpur have their sources in the neighbouring state of Selangor, with the middle reaches passing through the city before flowing through Selangor again and

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out to the sea. In view of that intimate link, freshwater resources are not treated as a separate entity and are still managed by the Selangor Water Works Department. Nevertheless, the highly urban and developed nature of Kuala Lumpur has a major impact on the river systems as they pass through the city. Therefore, it is important to consider the local effects, especially with regard to resource utilization and management.

The main objective of this work was to compare the results obtained from using the modified BCR sequential extraction method at different sediment depths and discuss the mobility potential of heavy metals with depth. To the best of our knowledge, no application of modified BCR sequential extraction scheme on the effect of trace element mobility potential at different column depths has been published before. Sediment certified reference material BCR 701 was also employed to test the extraction efficiency of the accelerated procedures. The metal contents of V, Pb, Cd, Cr, Co, Ni, Cu and Zn in the extracts were measured by inductively coupled plasma-mass spectrometry (ICP-MS). Also, the contamination factors and risk assessment code effects on surface samples are discussed.

## 2. Experiment

### 2.1. Sampling

For investigation of heavy metal mobility potential at different sediment levels in Sungai Buloh and Selat Melaka (Malacca Straits), seven different sampling stations were selected. Three samples were collected from Sungai Buloh near contaminated sites such as industries and factories, and four samples were taken from Selat Melaka downstream of Sungai Buloh, Selangor, one of the states in Malaysia in June 2009 (Table 1). The bottoms of some sampling sites were sandy so different amount of samples were taken from different stations. The samples were bagged, labelled and returned to the laboratory where they were cut to give 5 cm sub-samples. Large objects (including stones, pieces of brick, concrete and cinders) were removed and the remaining material was air-dried at a temperature lower than 30 °C under local exhaust ventilation to remove hazardous volatile components released, then sieved through a 1 mm nylon mesh. The air-dried samples were then coned and quartered (to ~20 g) and two portions of, 1 g sub-samples were removed for each method of sequential extraction.

### 2.2. Reagent

All reagents were of analytical grade unless otherwise stated. Double deionized water (Milli-Q Millipore 18.2 M $\Omega$ /cm resistivity) was used for all dilutions. All standards, reagent solutions and samples were kept in polyethylene containers. Acetic acid (glacial, 100% Fisher Scientific, Loughborough, Leicestershire, UK), hydroxylammonium chloride (ACROS Organics, NJ, USA), hydrogen peroxide (30% Fisher Scientific, Loughborough, Leicestershire, UK), and ammonium acetate and HNO<sub>3</sub> (65%, Suprapur Merck, Darmstadt, Germany) were of super pure quality. The plastic and glassware were cleaned by soaking in dilute HNO<sub>3</sub> (1 + 9) and were

rinsed with deionized water prior to use. Standard metal solutions (1000 mg/L) were purchased from Merck (Darmstadt, Germany) or prepared in the laboratory from pure metals. The extractants were prepared according to the following procedure.

**Solution I (acetic acid, 0.11 M):** Redistilled glacial acetic acid, 25 ± 0.2 mL, was added (in a fume cupboard), to about 500 mL of deionized water in a 1000 mL polyethylene volumetric flask and made up to the mark. 250 mL of this aliquot (0.43 M acetic acid) was diluted to 1.0 L to obtain an acetic acid concentration of 0.11 M.

**Solution II (hydroxylammonium chloride, 0.5 M, pH 1.5):** Hydroxylammonium chloride (34.75 g) was dissolved in deionised water. The solution was acidified with concentrated nitric acid to pH 1.5 and made up to 1000 mL with deionised water.

**Solution III (hydrogen peroxide, 8.8 M):** Hydrogen peroxide was used as supplied by the manufacturer, i.e., acid-stabilized to pH 2.0–3.0.

**Solution IV (ammonium acetate, 1.0 M):** Ammonium acetate (77.08 g) was dissolved in 900 mL of deionized water. The solution was acidified to pH 2.0 with concentrated nitric acid and made up to 1000 mL.

### 2.3. Apparatus

Trace element determination in the sediment samples was performed using an Agilent 7500a ICP-MS (Agilent Technologies, Japan) which was equipped with a Babington nebulizer. A glass, double-path spray chamber and a standard quartz torch operated at conditions listed in Table 2. A centrifuge instrument (Kubota 2420) was used to separate solid and liquid phases. The operating parameters for working elements were set as recommended by the manufacturer.

### 2.4. Pseudo total metal digestion

Pseudo total metal content was determined by digestion with mixture of *aqua regia* and HF. Vessels containing 1 g of the sediment and 20 mL of acid (15 mL HNO<sub>3</sub> + 5 mL HCl + 2 mL HF) were heated in a sand-bath heater. Digests were filtered through Whatman filter paper into 100 mL volumetric flasks (HF was used for digestion of metals that are bound to silicate materials).

### 2.5. Sequential extraction

Sequential extraction was performed using a three-stage modified procedure recommended by BCR plus the residual fraction (Table 3).

All extractions were carried out for 16 h (overnight) at room temperature, using a mechanical shaker. The extract was then separated from the solid residue by centrifugation for 20 min at 3000 rpm, and the resultant supernatant liquid was transferred into a polyethylene volumetric flask. The residue was washed by adding 20 mL of deionised water, shaken for 15 min on the end-over-end shaker, and centrifuged for 20 min at 3000 rpm. Subsequently, the supernatant was decanted.

**Table 1**  
Geographical locations of the sampling stations.

Sampling stations	Latitude	Longitude
1	03°14'47.34"N	101°28'10.38"E
2	03°16'02.64"N	101°27'.96"E
3	03°17'49.38"N	101°22'42.66"E
4	03°14'56.46"N	101°17'17.76"E
5	03°15'00.60"N	101°16'17.99"E
6	03°14'06.88"N	101°14'57.29"E
7	03°13'13.15"N	101°14'23.19"E

**Table 2**  
Instrumental parameters for trace element determination.

Parameters	Conditions
ICP-MS	Agilent 7500a
Auto sampler	ASX-500 series
RF power	1350 W
RF matching	1.6 V
Carrier gas flow rate	1.10 L/min
Peristaltic pump flow rate	0.1 rps

**Table 3**  
BCR three-stage sequential extraction scheme.

Extraction step	Reagent(s)	Nominal target phase(s)
1	HOAc (0.11 mol/L)	Soil solution, carbonates, exchangeable metals
2	NH <sub>2</sub> OH·HCl (0.1 mol/L)	Oxides Fe/Mn
3	H <sub>2</sub> O <sub>2</sub> (8.8 mol/L) then NH <sub>4</sub> OAc (1.0 mol/L) at pH 2	Organic matter and sulphides
Residual	HCl/HNO <sub>3</sub> + HF	Remaining, non-silicate bound metals

### 2.5.1. Steps of sequential extraction

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

**Step 2** (easily reducible fraction): 40 mL of a freshly prepared hydroxylammonium 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 the supernatant, and rinsing of residues were the same as described in Step 1.

**Step 3** (oxidizable fraction): the residue in 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 room temperature for 1 h with occasional manual shaking, followed by digestion at  $85 \pm 2^\circ\text{C}$  for another 1 h in a water bath. During the digestion, the centrifuge tube was loosely covered to prevent 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  $85 \pm 2^\circ\text{C}$  for another hour. Heating was continued as before until 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 the supernatant, and rinsing of residues were the same as described in Step 1.

**Step 4** (residual fraction): the residue from Step 3 was digested using a mixture of *aqua regia* and HF.

## 3. Results and discussion

### 3.1. Variation of metal distribution patterns with depth

To investigate the variation of distribution patterns of metals in the non-residual fractions with depth, seven sediment cores (with length between 0 and 45 cm) were collected at S1–S7. The triplicates of each sediment core at different length studied were used throughout this work.

#### 3.1.1. Fraction 1

According to step 1 of BCR scheme, the metals present in ionic form bound to carbonates and the exchangeable fraction were released as in Fraction 1. The element concentration variations in Fraction 1 at different depths for all sampling stations (S1–S7) are shown in Fig. 1. The concentration of metals were highest in the top sediments compared to other depth sub-samples for most of the elements at the seven sampling sites, except for Cr at station

S7 which was highest at 15 cm depth, and Ni at station S3 that dominantly increased from top going down. Variation trends of concentration for each element in the seven sample cores were approximately similar, indicating a normal decrease from top to lower level of the sample cores.

The surface enrichment may be due to the contamination deposited from the surface waters, which also indicates that the pollution is of recent years. This is because the pollutants are always absorbed into top sediment first, and then sinks into deeper positions by chemical exchange.

The fact that much higher concentrations of V, Pb, Cd, Ni, Cu, Zn and Cr in the top sediments found at stations S2 and S3 indicating that these two stations suffered from more severe pollution compared to other stations.

The discrimination became small at higher depth, especially of deeper than 15 cm. This phenomenon may be interpreted as the elements in Fraction 1 are mainly caused by pollution in the top sediments. At increasing depths, the effects of pollution become slighter and element distribution mainly depends the geographical location of the sediments themselves.

#### 3.1.2. Fraction 2

In the step 2 of BCR scheme, metals bound to amorphous Fe and Mn oxides and hydroxides were leached as shown in Fraction 2. The element concentration variations in Fraction 2 with depths at S1–S7 are shown in Fig. 2. Higher metal concentrations were found in the top layer of the sediments for most elements except for V at S1. A dominant fluctuation has obtained for V in this station. In this fraction, high concentrations of some elements like Pb, Cd, Cr, Ni and Zn have been found in S2 and S3 that should be due to industrial pollution in this area. Pb, Cd and Cu were also high range at station 1. We can see an exception for Cr at station 7, which can be interpreted as a special Cr contamination from the past few years.

The results show that larger amounts of elements may be sorbed by more Fe–Mn oxides in the top sediments than at the deeper depths. That could mean that the reductive dissolution of Fe–Mn oxides will occur at deeper positions in the absence of significant sulphide which could fix the Fe and Mn as sulphide phase followed by precipitation upon crossing the oxic/anoxic boundary. The freshly formed Fe–Mn oxides may also scavenge a significant amount of upwards diffusing heavy metals.

The discrimination became smaller with increasing depth for Zn and Ni.

#### 3.1.3. Fraction 3

In step 3, metals bound to organic matter and sulphides were separated. The element concentration variations in Fraction 3 with depths at S1–S7 are shown in Fig. 3. The variations of element concentrations in this fraction were more complex than in the two previous fractions. There was no evident that could be concluded from the results, but some useful information could be obtained. The concentrations of all elements except V and Co at stations 2 and 3 are higher than that of the other stations. The similar distribution pattern can be seen at station 1 for Pb, Cd and Cu. Elements obtained in Fraction 3 mainly bound to various forms of organic matter by complexation and bound to natural organic matter by bioaccumulation in certain living organisms through different ways. So, the variation of elements in this fraction became more complex and irregular than that of Fractions 1 and 2.

### 3.2. Reproducibility and accuracy of the method

To evaluate the reproducibility and accuracy of the method, a certified reference material (CRM BCR 701) was subjected to the BCR protocol. The results are listed in Table 4.

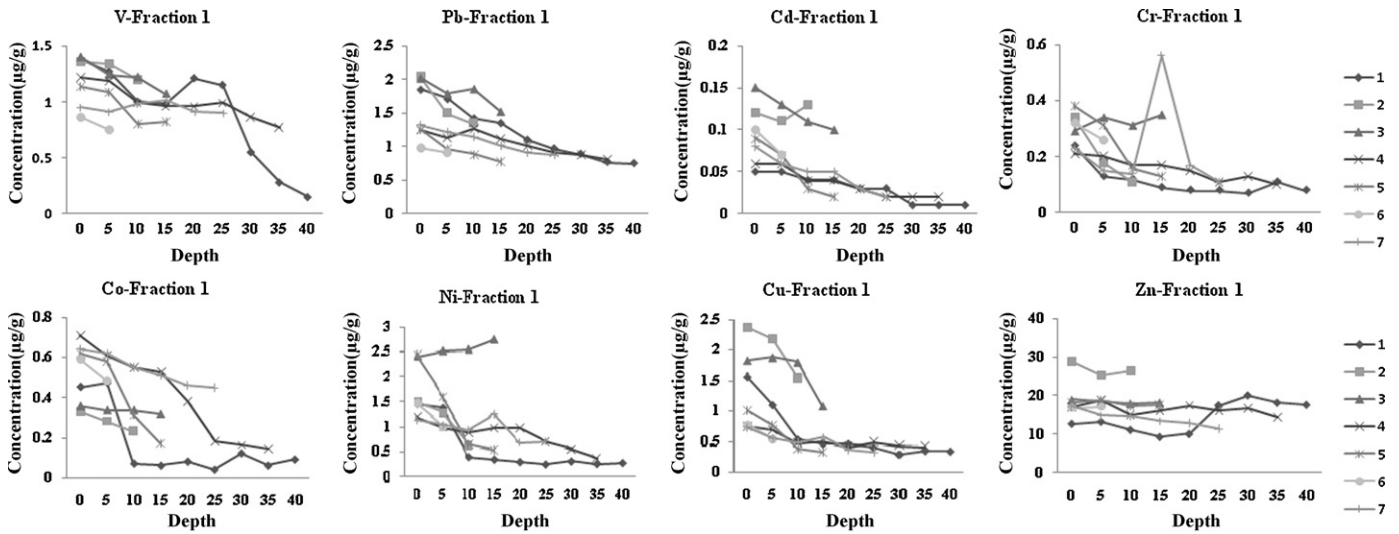


Fig. 1. Concentration variation of elements in different depths for Fraction 1.

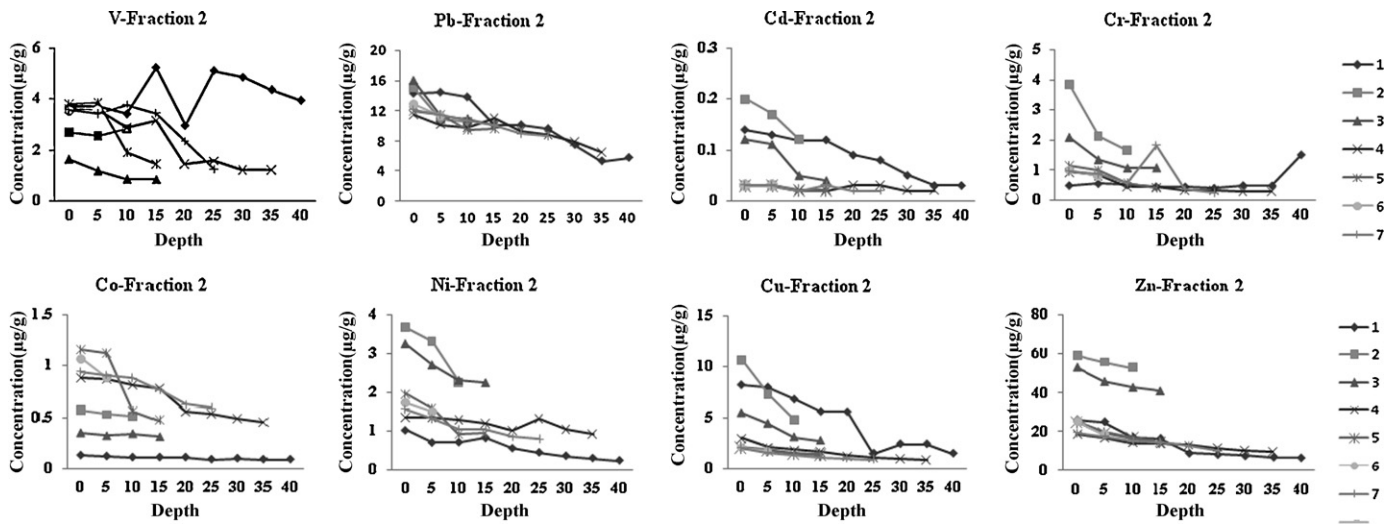


Fig. 2. Concentration variation of elements in different depths for Fraction 2.

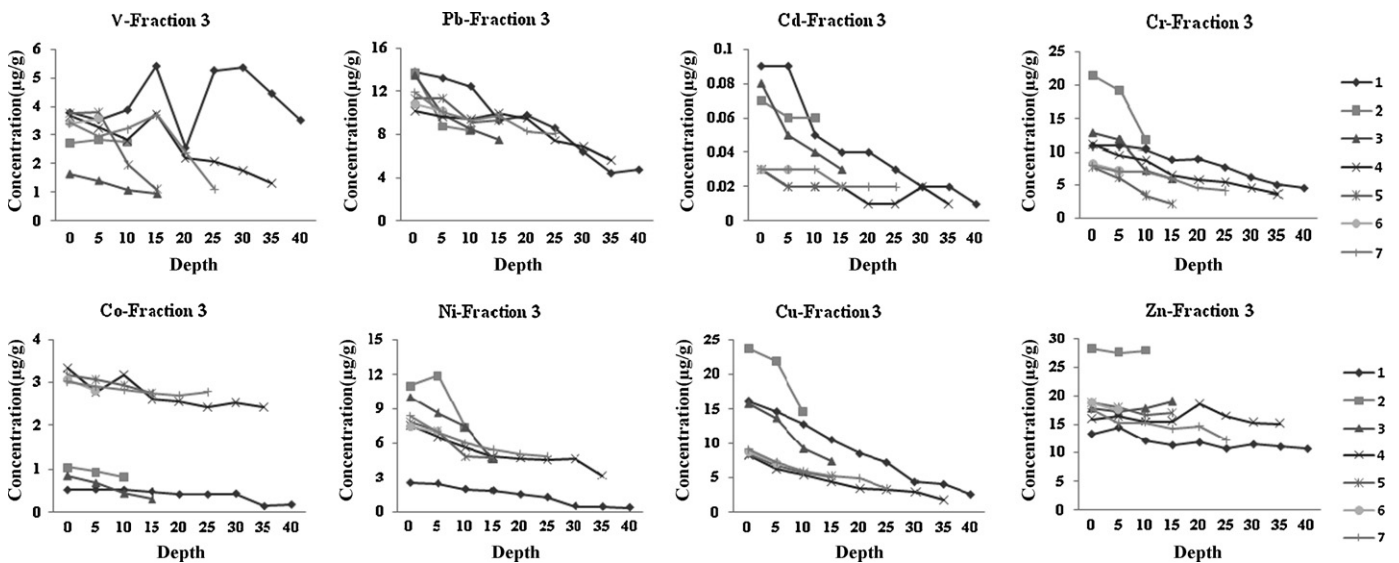


Fig. 3. Concentration variation of elements in different depths for Fraction 3.



**Table 4**  
Comparison between certified and found values for extractable trace elements in lake sediment reference material BCR CRM 701 ( $\mu\text{g/g}$ ).

	Cd	Cr	Cu	Ni	Pb	Zn
Step 1						
Certified	7.34 $\pm$ 0.35	2.26 $\pm$ 0.16	49.3 $\pm$ 1.7	15.4 $\pm$ 0.9	3.18 $\pm$ 0.21	205 $\pm$ 6
Found	7.11 $\pm$ 0.43	2.16 $\pm$ 0.14	48.5 $\pm$ 2.2	14.7 $\pm$ 1.1	3.01 $\pm$ 0.29	207 $\pm$ 11
Step 2						
Certified	3.77 $\pm$ 0.28	45.7 $\pm$ 2.0	124 $\pm$ 3	26.6 $\pm$ 1.3	126 $\pm$ 3	114 $\pm$ 5
Found	3.59 $\pm$ 0.37	43.9 $\pm$ 3.1	117 $\pm$ 7	26.4 $\pm$ 1.8	122 $\pm$ 7	109 $\pm$ 9
Step 3						
Certified	0.27 $\pm$ 0.06	143 $\pm$ 7	55.2 $\pm$ 4.0	15.3 $\pm$ 0.9	9.3 $\pm$ 2.0	45.7 $\pm$ 4.0
Found	0.27 $\pm$ 0.09	139 $\pm$ 9	53.5 $\pm$ 3.7	15.0 $\pm$ 0.4	8.9 $\pm$ 1.6	42.9 $\pm$ 4.7

### 3.3. Sequential extraction results in the surface sediments

The metal concentrations in surface sediments of the river and marine sediment samples from each extraction step are shown in Table 5. The discussion on the distribution patterns of elements is divided into five groups depending on the degree of their association with the different phases. V and Cr were found to be present mainly in the residual fraction, while Co and Ni were found in the oxidisable fraction. In addition, Zn and Pb were found in a group with the large proportion of the total concentration presenting in the easily reducible fraction, also Cd was found in the acid extractable/exchangeable fraction, moreover, large amounts of Cu were obtained in oxidisable fraction at stations 1–3 and residual fraction from stations 4 to 7.

#### 3.3.1. Vanadium and chromium

In this study, the results show that V and Cr are mainly found in the residual fraction (Fig. 4), representing 73.9–86.52% and 52.78–75.44%, respectively. The phase distribution of V and Cr in this study is similar to the results reported by Yuan et al. [16], indicating that V and Cr were mostly retained in the residual fraction. Elements associated with the residual fraction are likely to be incorporated in aluminosilicate minerals, and so are unlikely to be released to pore-waters through dissociation. Less than 10%, 10% and 5% of V have been found in oxidisable, easily reducible and exchangeable fractions, respectively. The highest amount of V was obtained at S3 in residual fraction. However, the amount of Cr in Fractions 1, 2 and 3 was only less than 1%, 8% and 40%, respectively at all stations.

Furthermore, Cr found at S5 showed the highest portion in residual fraction. In this case, the portion of oxidisable fraction is noticeable too.

#### 3.3.2. Cobalt and nickel

The distribution patterns of Co and Ni are illustrated in Fig. 4. Co and Ni were distributed in all four fractions of the sediment phases, but the dominant portion was obtained in the oxidisable fraction. The dominant phase in the oxidisable fraction accounted for more than 56% of the total concentration of elements at stations S4–S7 and less than 50% at stations S1–S3. There was a portion between 10% and 20% in exchangeable and residual fraction at all stations except Co at station S1. The considerable proportion of total Ni concentration (about 50%) was in the oxidisable fraction at all stations except S1 that was found in residual fraction. However, Ni showed less than 17% of total Ni in Fractions 1 and 2 at all stations.

#### 3.3.3. Zinc and lead

The dominant portion of Zn and Pb were in easily reducible fraction (iron–manganese oxide fraction). Zn showed a variation between 28% and 40% in Fraction 2 while a noticeable amount of this element was observed in exchangeable fraction at S1–S3. Although the highest concentration of Pb was obtained in Fraction 2, very

similar results were found for Fractions 1 and 3. Less Pb content was obtained in exchangeable fraction (>5%).

#### 3.3.4. Cadmium

The levels of Cd in sediments and sludge have been the focus of much concern for a long time due to its high toxicity. Several sequential extraction procedures, including the BCR protocol have been used to obtain information on the distribution of Cd in sediment [17–19]. Not only sediments, but also other samples such as soil [20,21] and fly-ash samples [22], have been determined for the concentrations of Cd phase distribution by sequential extraction methods. In this study, Cd was also detected in the marine sediments following the BCR sequential extraction. The results of sequential extraction for Cd are illustrated in Fig. 4.

As we can see, the variation of Cd was more significant than other elements. For example, more than 33% of the total Cd concentration was observed in exchangeable fraction at stations S3–S7 while less than 23% was obtained at stations S1 and S2. The highest concentrations of total Cd were found in easily reducible fraction at stations S1 and S2. Noticeable portion of Cd was found in residual fraction at stations S4–S7.

#### 3.3.5. Copper

Cu showed exactly two different patterns in river and marine sediments. The high portion of Cu was obtained in oxidisable fraction at stations S1–S3 (Sungai Buloh River sediments) and residual fraction at stations S4–S7 (the Straits of Malacca sediments). About 30% of total Cu was found at S1–S3 in residual fraction and oxidisable fraction at stations S4–S7.

### 3.4. Pseudo total metal digestion

The results of pseudototal metal digestion are presented in Table 5 and the amounts of heavy metals found at seven sampling stations are compared in Table 6.

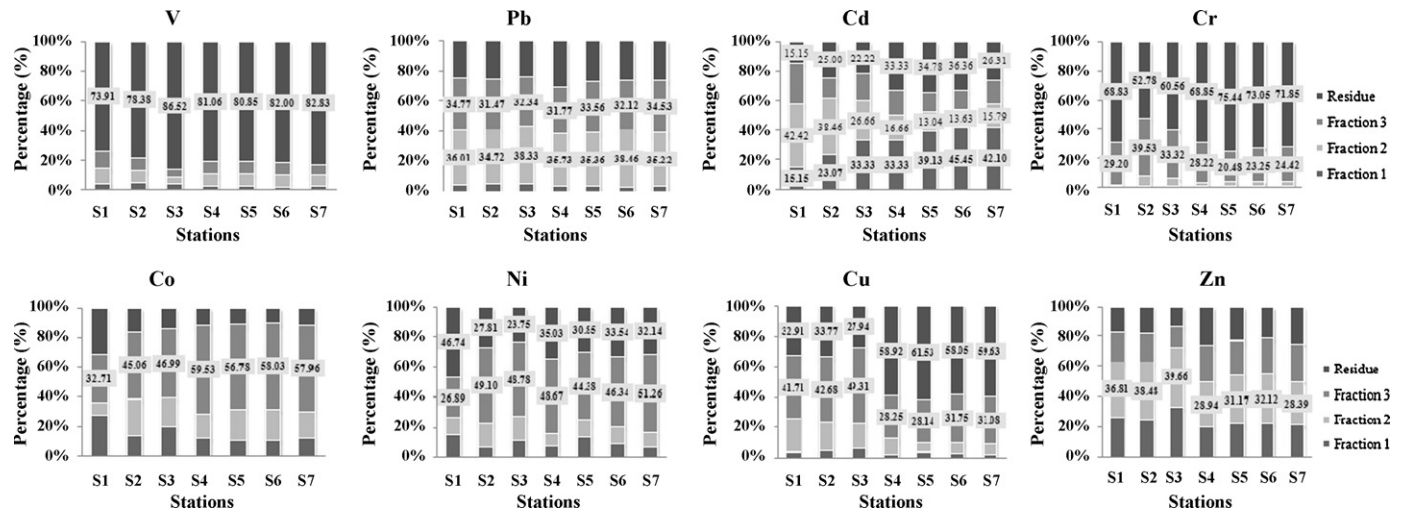
The highest total amounts of elements after pseudototal metal digestion were obtained for Cr, Ni, Cu, Zn, Cd and Pb at station S2. This is due to the sediment sample was collected exactly from outside a metal factory. It showed that the production of metallic tube industries play an important role in river pollution. Also, high concentrations of V and Co were obtained in samples taken from marine locations. As we know, one of the major sources of V and Co are oil and petrol products. Therefore, these sample matrices have been contaminated by shipping industries, fishing industries or boating which are the common anthropogenic activities in this area. The contamination in Sungai Buloh sediments increased from upstream to downstream. Nevertheless, high element contamination was obtained at station S2 due to the metal industry. In addition, much of the municipal wastewater is discharged into this river, thus increasing river pollution.

**Table 5**  
Concentration of metals by modified BCR SEP ( $\mu\text{g/g}$ ).

	V	Cr	Co	Ni	Cu	Zn	Cd	Pb
Station no. 1								
Fraction 1	1.38	0.24	0.45	1.45	1.55	18.58	0.05	1.85
Fraction 2	3.68	0.49	0.13	1.02	8.22	25.99	0.14	14.25
Fraction 3	3.80	10.89	0.53	2.52	16.06	13.36	0.09	13.76
Residue	25.11	25.67	0.51	4.38	12.67	12.67	0.05	9.71
Three step + residue	33.97	37.29	1.62	9.37	38.50	70.60	0.33	39.57
Pseudo-total	34.17	37.83	1.59	9.55	39.14	68.75	0.35	40.14
Recovery (%)	99.41	98.57	101.88	98.11	98.36	102.69	94.28	98.58
$C_f$	0.35	0.45	2.17	1.14	2.03	4.57	5.60	3.07
RAC (%)	4.06	0.64	27.77	15.47	4.02	26.31	15.15	4.67
Station no. 2								
Fraction 1	1.36	0.34	0.33	1.49	2.37	36.96	0.12	2.04
Fraction 2	2.67	3.84	0.57	3.68	10.69	58.74	0.20	15.06
Fraction 3	2.70	21.52	1.05	11.00	23.67	28.22	0.07	13.65
Residue	24.4	28.73	0.38	6.23	18.73	28.73	0.13	12.62
Three step + residue	31.13	54.43	2.33	22.40	55.46	152.65	0.52	43.37
Pseudo-total	31.88	55.04	2.28	22.26	55.96	157.31	0.55	43.66
Recovery (%)	97.64	98.89	102.19	100.62	99.10	97.03	94.54	99.33
$C_f$	0.27	0.89	5.13	2.59	1.96	4.31	2.69	2.43
RAC	4.36	0.62	14.16	6.65	4.27	24.21	23.07	4.70
Station no. 3								
Fraction 1	1.40	0.29	0.36	2.40	1.82	44.03	0.15	2.02
Fraction 2	1.62	2.07	0.35	3.24	5.47	53.16	0.12	15.99
Fraction 3	1.65	12.87	0.86	10.02	15.81	17.86	0.08	13.49
Residue	29.99	23.39	0.26	4.88	8.96	18.96	0.10	10.21
Three step + residue	34.66	38.62	1.83	20.54	32.06	134.01	0.45	41.71
Pseudo-total	35.21	38.17	1.91	21.02	32.61	137.29	0.48	42.10
Recovery (%)	98.43	101.17	95.81	97.71	98.31	97.61	93.75	99.07
$C_f$	0.15	0.65	6.03	3.21	2.57	6.06	3.50	3.08
RAC	4.04	0.75	19.67	11.68	5.67	32.85	33.33	4.84
Station no. 4								
Fraction 1	1.22	0.21	0.71	1.19	0.74	13.16	0.06	1.25
Fraction 2	3.61	0.94	0.88	1.33	2.98	18.86	0.03	11.44
Fraction 3	3.65	11.11	3.34	7.53	8.20	16.03	0.03	10.17
Residue	36.3	27.10	0.68	5.42	17.10	17.11	0.06	9.15
Three step + residue	44.78	39.36	5.61	15.47	29.02	65.16	0.18	32.01
Pseudo-total	45.27	39.77	5.59	15.83	29.66	65.48	0.19	32.49
Recovery (%)	98.91	98.96	100.35	97.72	97.84	99.49	94.73	98.52
$C_f$	0.23	0.45	7.24	1.85	0.69	2.80	2.00	2.49
RAC	2.72	3.74	12.65	7.69	2.55	20.19	33.33	3.90
Station no. 5								
Fraction 1	1.14	0.38	0.62	2.43	1.01	17.74	0.09	1.26
Fraction 2	3.81	1.14	1.16	1.96	2.04	24.82	0.03	11.98
Fraction 3	3.75	7.65	3.18	7.87	8.31	18.90	0.03	11.37
Residue	36.73	28.17	0.64	5.47	18.17	18.17	0.08	9.27
Three step + residue	45.43	37.34	5.60	17.73	29.53	79.63	0.23	33.88
Pseudo-total	45.75	37.90	5.93	17.42	29.88	80.19	0.23	33.62
Recovery (%)	99.30	98.52	94.43	101.78	98.82	99.30	100.00	100.77
$C_f$	0.23	0.32	7.75	2.24	0.62	3.38	1.87	2.65
RAC	2.51	1.01	11.07	13.70	3.42	22.27	39.13	3.71
Station no. 6								
Fraction 1	0.86	0.32	0.59	1.48	0.77	17.33	0.10	0.98
Fraction 2	3.51	0.99	1.07	1.74	2.02	25.10	0.03	12.91
Fraction 3	3.41	8.24	3.07	7.42	8.69	18.82	0.03	10.78
Residue	35.44	25.89	0.56	5.37	15.89	16.89	0.06	8.89
Three step + residue	43.22	35.44	5.29	16.01	27.37	78.14	0.22	33.56
Pseudo-total	43.64	35.41	5.55	15.89	27.52	79.01	0.23	33.97
Recovery (%)	99.03	100.08	95.31	100.75	99.45	98.89	95.65	98.79
$C_f$	0.22	0.36	8.44	1.98	0.72	3.62	2.66	2.77
RAC	1.98	0.90	11.15	9.24	2.81	22.17	45.45	2.92
Station no. 7								
Fraction 1	0.95	0.23	0.64	1.14	0.72	14.52	0.08	1.32
Fraction 2	3.57	0.97	0.94	1.55	1.96	19.61	0.03	12.15
Fraction 3	3.41	7.89	3.02	8.31	8.97	17.71	0.03	11.91
Residue	38.27	23.21	0.61	5.21	17.21	17.21	0.05	9.11
Elements Concentrations in total digestion								
V	S7>S5>S4>S6>S3>S1>S2							
Cr	S2>S4>S3>S5>S1>S6>S7							
Co	S5>S4>S6>S7>S2>S3>S1							
Ni	S2>S3>S5>S7>S6>S4>S1							
Cu	S2>S1>S3>S5>S4>S7>S6							
Zn	S2>S3>S5>S6>S7>S1>S4							
Cd	S2>S3>S1>S5>S6>S4>S7							
Pb	S2>S3>S1>S7>S6>S5>S4							

**Table 5**  
(continued)

	V	Cr	Co	Ni	Cu	Zn	Cd	Pb
Three step + residue	46.20	32.3	5.21	16.21	28.86	69.05	0.19	34.49
Pseudo-total	46.74	32.44	5.19	16.97	28.37	69.80	0.18	34.92
Recovery (%)	98.84	99.56	100.38	95.52	101.72	98.92	105.55	98.76
$C_f$	0.20	0.39	7.54	2.11	0.67	3.01	2.80	2.78
RAC	2.05	0.71	12.28	7.03	2.49	21.02	42.10	3.82



**Fig. 4.** The average percentage of element speciation in different stations using modified BCR SEP method.

**3.5. Internal check recovery**

An internal check was performed on the results of the sequential extraction by comparing the total amount of metal extracted by different reagents during the sequential extraction procedure with the results of the total digestion. The recovery of the sequential extraction method was calculated as follows:

$$\text{Recovery} = \left[ \frac{C_{\text{Fraction 1}} + C_{\text{Fraction 2}} + C_{\text{Fraction 3}} + C_{\text{Residue}}}{C_{\text{total digestion}}} \right] \times 100$$

The results shown in Table 5 indicate that the sums of the four fractions are in good agreement with the total digestion results, with satisfactory recoveries (94.43–105.55%) and the method used is reliable and repeatable.

**3.6. Environmental implications**

To study heavy-metal retention in sediment samples, the individual contamination factors ( $C_f$ ) of elements and risk assessment code (RAC) in Sungai Buloh and Selat Melaka samples were calculated (Table 5).

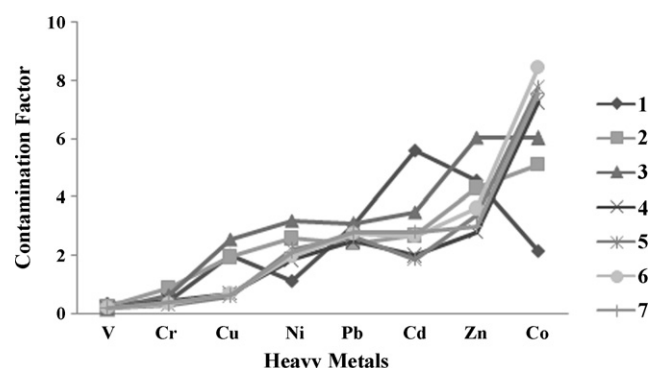
**Table 6**  
Comparison of total element digestion using pseudo total metal digestion method.

Elements	Concentrations in total digestion
V	S7 > S5 > S4 > S6 > S3 > S1 > S2
Cr	S2 > S4 > S3 > S5 > S1 > S6 > S7
Co	S5 > S4 > S6 > S7 > S2 > S3 > S1
Ni	S2 > S3 > S5 > S7 > S6 > S4 > S1
Cu	S2 > S1 > S3 > S5 > S4 > S7 > S6
Zn	S2 > S3 > S5 > S6 > S7 > S1 > S4
Cd	S2 > S3 > S1 > S5 > S6 > S4 > S7
Pb	S2 > S3 > S1 > S7 > S6 > S5 > S4

**3.6.1. Contamination factor ( $C_f$ )**

The determination of heavy-metal contamination factor is an important aspect that indicates the degree of heavy metals risk to the environment in relation with its retention time. A high contamination factor of heavy metals shows low retention time and high risk to the environment. The individual contamination factor ( $C_f$ ) of heavy metals was used to estimate the relative retention time of heavy metals retained in the sediment. It is determined by dividing the sum of each heavy metal concentration in the mobile phase (non-residue phase) by its concentration in the residual phase.

Fig. 5 shows the estimated contamination factors of each metal in the surface samples at all stations. The calculated factors in both types of sediment show the highest  $C_f$  and the ability of Cd, Co, Zn and Pb to be released from Sungai Buloh (S1–S3), whereas V and Cr show the lowest. The residual concentration of any heavy metal is considered a non-mobile fraction and is an important part in influencing the mobility nature of the heavy metal. The combined effect of Cd, Zn, and Pb in high concentrations and with high mobility



**Fig. 5.** Estimated contamination factor of each metal in the surface samples at 7 stations.

**Table 7**  
Comparison of RAC values for all stations and elements.

	V	Cr	Co	Ni	Cu	Zn	Cd	Pb
S1	L	L	M	M	L	M	M	L
S2	L	L	M	L	L	M	M	L
S3	L	L	M	M	L	H	H	L
S4	L	L	M	L	L	M	H	L
S5	L	L	M	M	L	M	H	L
S6	L	L	M	L	L	M	H	L
S7	L	L	M	L	L	M	H	L

potential shows the increased possible risk of these metals to the environment (S1–S3).

The highest contamination factor was obtained for Co, Zn and Pb in the sediment samples obtained from the Straits of Malacca sediments (S4–S7), while the lowest was found for V and Cr, similar to Sungai Buloh sediments.

### 3.6.2. Risk assessment code (RAC)

The risk assessment code, defined as the fraction of metal exchangeable and/or associated with carbonates (% F1 for BCR), was determined for the eight trace metals, and the values interpreted in accordance with the RAC classifications. This classification is described by Perin et al. [23].

Metals are bound to different sediment fractions, with the binding strength determining their bioavailability and the risk associated with their presence in aquatic systems. The risk assessment code (RAC) was determined based on the percentage of the total metal content that was found in the first sediment fraction in BCR method (% F1). This indicates that the metals are weakly bound to the solid phase. Hence, the metals pose a greater risk to the aquatic environment due to their greater potential [24]. When this percentage mobility is less than 1%, the sediment has no risk to the aquatic environment. Percentages of 1–10% reflect low risk, 11–30% medium risk, and 31–50% high risk. Above 50%, the sediment poses a very high risk and is considered dangerous, with metals easily able to enter the food chain [23,24].

Table 5 shows the results of RAC with values given as percentage of the fraction soluble in acid and carbonate fraction (% F1).

In general, the sediments show low risk for V, Cr, Cu and Pb with RAC values less than 10%, so, there is not any significant metal mobility for these element. A medium risk is indicated for Co, Zn (except at S3), Cd at S1 and S2 and Ni at S1, S3 and S5 that it can be noticeable in the early future. Zn at S3 and Cd at S3–S7 show high risk for our sediment samples. Therefore, a significant remediation must be applied for Zn and Cd mobilization as soon as possible. From the selected samples there are no elements at very high risk conditions. Table 7 shows the comparison of RAC values for all stations and elements.

## 4. Conclusion

The BCR sequential extraction method was applied to the analysis of metal in order to obtain a distribution pattern in the Sungai Buloh (river) sediments and Selat Melaka, Selangor, Malaysia (marine). To investigate the variations of distribution patterns of metals in the non-residual fractions with depth, seven sediment cores (with lengths between 0 and 45 cm) were collected at S1–S7. In Fraction 1, concentration variation trends for each element in the seven sample cores were approximately similar, indicating a normal decrease from top downwards.

The surface enrichment may be due to contamination deposited from surface waters, which also indicates that the pollution is of recent years. This is because pollution is always absorbed in the top sediments at first, and then sinks into deeper positions by chemical exchange. In Fraction 2, the results show that larger amounts

of the elements may be absorbed by more Fe–Mn oxides in the top sediments than at the deeper positions. That could mean that the reductive dissolution of Fe–Mn oxides will occur at deeper positions in the absence of significant sulphide which could fix the Fe and Mn as sulphide phase, followed by precipitation upon crossing the oxic/anoxic boundary. The freshly formed Fe–Mn oxides may also scavenge a significant amount of upwards diffusing heavy metals. In Fraction 3, the concentrations of all elements except V, As and Co at stations 2 and 3 are higher than other stations. Similar results are seen at station 1 for Pb, Cd and Cu. Elements in Fraction 3 are mainly bound to various forms of organic matter by complexation and to natural organic matter by bioaccumulation in certain living organisms through different ways. So the variation of elements in this fraction became more complex and irregular than that in Fractions 1 and 2.

The discussion on element distribution patterns is divided into five groups depending on the degree of their association with the different phases. V and Cr are mainly in the residual fraction, while Co and Ni were distributed in all four fractions of the sediment phases, but the dominant portion was obtained in the oxidisable fraction. The dominant portion of Zn and Pb were in easily reducible fraction (iron–manganese oxide fraction). The variation of Cd was more significant than other elements. For example, more than 33% of total Cd concentration was obtained in exchangeable fraction at S3–S7 while less than 23% was obtained at S1 and S2. The highest concentrations of total Cd were found in easily reducible fraction at S1 and S2. Noticeable portion of Cd was found in residual fraction at S4–S7. The high portion of Cu was obtained in oxidisable fraction at S1–S3 (Sungai Buloh River sediments) and residual fraction at S4–S7 (the Straits of Malacca sediments).

To study heavy metal retention in sediment samples, the individual contamination factors (Cf) of elements and Risk Assessment Code (RAC) were calculated. The calculated contamination factor showed the highest Cf and ability of Cd, Co, Zn and Pb to be released from Sungai Buloh (S1–S3), whereas V and Cr showed the lowest. In the samples from the Straits of Malacca sediments (S4–S7), the highest contamination factors were obtained for Co, Zn and Pb, while the lowest were found for V and Cr, similar to Sungai Buloh sediments. The sediments showed a low risk for V, Cr, Cu and Pb with RAC values less than 10%, but a medium risk indicated for Co, Zn (except S3), Cd at S1 and S2 and Ni at S1, S3 and S5. Zn at S3 and Cd at S3–S7 showed a high risk for the sediment samples. There were no elements of very high risk conditions in the selected samples.

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