

# Potentially Toxic Metal and Metalloid Fractionation Contamination in Sediments of Daya Bay, South China Sea

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## Abstract

The metal profiles in sediments of the Daya Bay (DYB) in China were established using sequential extraction protocols proposed by the European Community Bureau of Reference (BCR). The surface sediment samples from 23 representative stations were collected in 2011 and were analysed to evaluate the mobility and bioavailability of a suite of potentially toxic metals (Cr, Cu, Ni, Zn, Pb and Cd) and metalloid (As). The obtained ranking order of migration and transformation, and the degree of pollution was Pb > Cd > Cu > Zn > Ni > Cr > As. Among these elements, Pb is considered to pose a serious threat to human health and ecological environment due to its significant percentage in non-residual form. The ratios of secondary and primary phases showed that studied sediments are moderately to heavily polluted with Cu and Zn, and Cd and Pb respectively. The levels of association between the variables (metal-metalloid) at each step of sequential extractions were evaluated with multivariate statistical analysis, including correlation analysis and principal components analysis. With these analyses, the possible sources of potential pollution were deduced. The correlation analysis revealed that Total Organic Carbon content is the most important influencing factor affecting the distribution of potentially toxic elements in Daya Bay. The principal components analysis (PCA) suggested that the studied elements in DYB area originate primarily from natural weathering and secondly from industrial wastewater and aquaculture waste water.

## Keywords

*Toxic elements, metal fractionation, sequential extraction, risk assessment, sediment, Daya Bay*

## Introduction

The pollution of the natural environment by heavy metals is recently a topic of much discussion; and the issue of potentially toxic metal pollution in coastal marine sediments has received much more attention from researchers over the past few decades. Due to dense anthropogenic activities as well as increasing usage of industrial products, a huge amount of waste products is discharged into water bodies without proper treatment. Coastal marine sediments not only function as a reservoir for metals, but also as a natural and pollution source of metals.<sup>1</sup> These in particular have drawn much attention due to their biological accumulation, toxicity and persistence once the concentrations surpass certain thresholds in the sediments, resulting in potential long-term exposure of humans and organisms to these metals. The mobility and toxicity of metals associated with sediments are generally affected by metal speciation and sediment composition.<sup>2</sup>

Although a number of dredging and remediation actions

are focused on metals, successful projects rely on the good understanding of the behaviour of contaminants when bottom sediments are dredged, brought to the surface and exposed to different environmental conditions. Total metal concentrations can be used as an indicator for environmental assessment, however they cannot be used to assess bioavailability and the environmental/human health risks.<sup>3</sup> The risks posed by hazardous substances in dredged sediments are determined by their “mobile” and “available” concentrations.<sup>4</sup> Thus, other than measurement of total concentrations of metals in sediments, determination of their geochemical fractionation is also very important for assessing their mobility, bioavailability and potential toxicity.

Our main objectives were (a) to assess the concentration and speciation of toxic metals in the sediments of the Daya Bay, and (b) to carry out a preliminary evaluation of the potential environmental risks. The results from this study will provide a better understanding of the risks of metals in the sediments of the studied region.

Daya Bay, located in the northeast part of the South China Sea, has become a vital economy development zone. It is composed of a series of sub-basins, including Dap-

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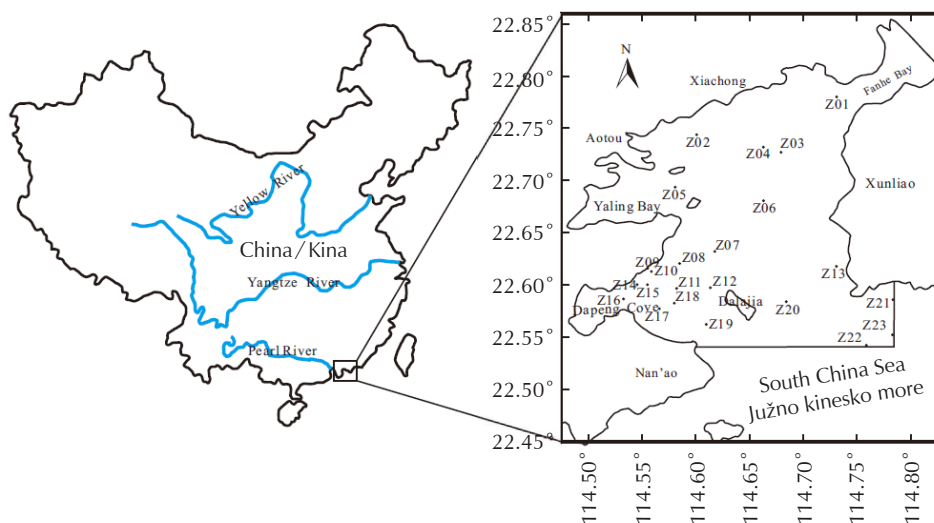


Fig. 1 – Sampling stations in studied regions  
Slika 1 – Lokacije na kojima su uzimani uzorci

eng Cove, Fanhe Bay and Yaling Bay. Since the 1980s, the population number as well as aquacultural and industrial pollution along the coastline and harbours have increased dramatically.<sup>5,6</sup> In this region, the distribution of metals and their speciation in different fractions in the sediments have not been fully studied so far, and comprehensive multi-factor characteristics analyses should be conducted.

## Materials and methodology

### Sampling and sediment pretreatment

The surface sediments samples were taken around the Daya Bay from May to June in 2011, and collected in brown glass bottles and polyethylene bags, and stored at low temperature ( $-20\text{ }^{\circ}\text{C}$ ) for further experiments. The sampling stations are shown in Fig. 1. The concentrations of Cr, Cu, Ni, Zn, Pb, As and Cd were measured in the laboratory using standard methods.

### Analysis

#### Total concentrations

The total concentrations of Cr, Ni, Cu, Pb, Zn, Cd and As were detected by inductively coupled plasma-mass spectrometry (ICP-MS).

#### Morphological analysis

The modified European Community Bureau of Reference (BCR) sequential extractions method was used to analyse the speciation of heavy metals in this paper.<sup>7,8</sup> The blanks were analysed at the same time.

#### Step 1, Fraction 1 (F1, acid soluble fraction)

Subsamples (0.5 g) of dry sediment and 30 ml of acetic acid were added to a 50 ml Pyrex tube. The tubes containing the mixtures were shaken for 20 hours at room temperature ( $22\pm 2\text{ }^{\circ}\text{C}$ ) and extracts were separated from the

residues by centrifugation at 3500 rpm. The supernatants were removed and the residues washed with 10 ml distilled  $\text{H}_2\text{O}$ , shaken for an additional 10 minutes and centrifuged for 20 minutes at 3500 rpm. The supernatants were removed carefully and completely without loss of residues.

#### Step 2 Fraction 2 (F2, reducible fraction)

The residues from Step 1 were re-suspended by adding 20 ml of  $0.1\text{ mol l}^{-1}\text{ NH}_2\text{OHHCl}$  ( $\text{pH} = 2.0$ ) and the extraction was carried out as described in Step 1.

#### Step 3 Fraction 3 (F3, oxidizable fraction)

20 ml of  $8.8\text{ mol l}^{-1}\text{ H}_2\text{O}_2$  ( $\text{pH} 2.0 - 3.0$ ) were added drop-by-drop to the residues from Step 2. The tubes were sealed with caps and the residues sequentially digested for 2 hours at room temperature and 1 hour at  $85\text{ }^{\circ}\text{C}$  in a water bath. The digestion mixtures were concentrated by evaporation to the final volumes of 2 – 3 ml. Step 3 was repeated twice and 25 ml of  $1\text{ mol l}^{-1}\text{ NH}_4\text{C}_2\text{H}_3\text{O}_2$  ( $\text{pH} = 2.0$ ) was added to the cool residues, which were separated and rinsed as described in Step 1.

#### Step 4 Fraction 4 (F4, residual fraction)

The residues in Step 3 were transformed to a polytetrafluoroethylene beaker and 25.00 ml nitrate, 2.00 ml hydrofluoric acid and 2.00 ml perchloric acid were added and digestion was carried out until the residues were almost dry. Residues were re-dissolved in nitrate (1 %), and prepared for further measurement. The metal concentrations in the extracts obtained at each step were determined using an atomic absorption spectrophotometer.

#### Particle size and total organic carbon

The analysis of granularity and Total Organic Carbon (TOC) were performed according to the specifications for marine monitoring (GB17378-2007).

### Quality control

Quality control was assured in the same way as the analysis of a marine sediment reference material (Offshore Marine Sediment, GBW 07314) with both duplicate and parallel samples. The duplicates showed a difference of <math><10\%</math>, while the spiked additions (blanks and samples) gave recovery percentages ranging from 95 % to 106 %.

## Results

### Distribution of total metals

According to Shepard's sediment granularity classification,<sup>9</sup> the average clay, silt and sand contents in all samples are 4.9 %, 77.0 % and 18.1 %, respectively. The average percentages of clayey silt and sandy silt in silt samples are

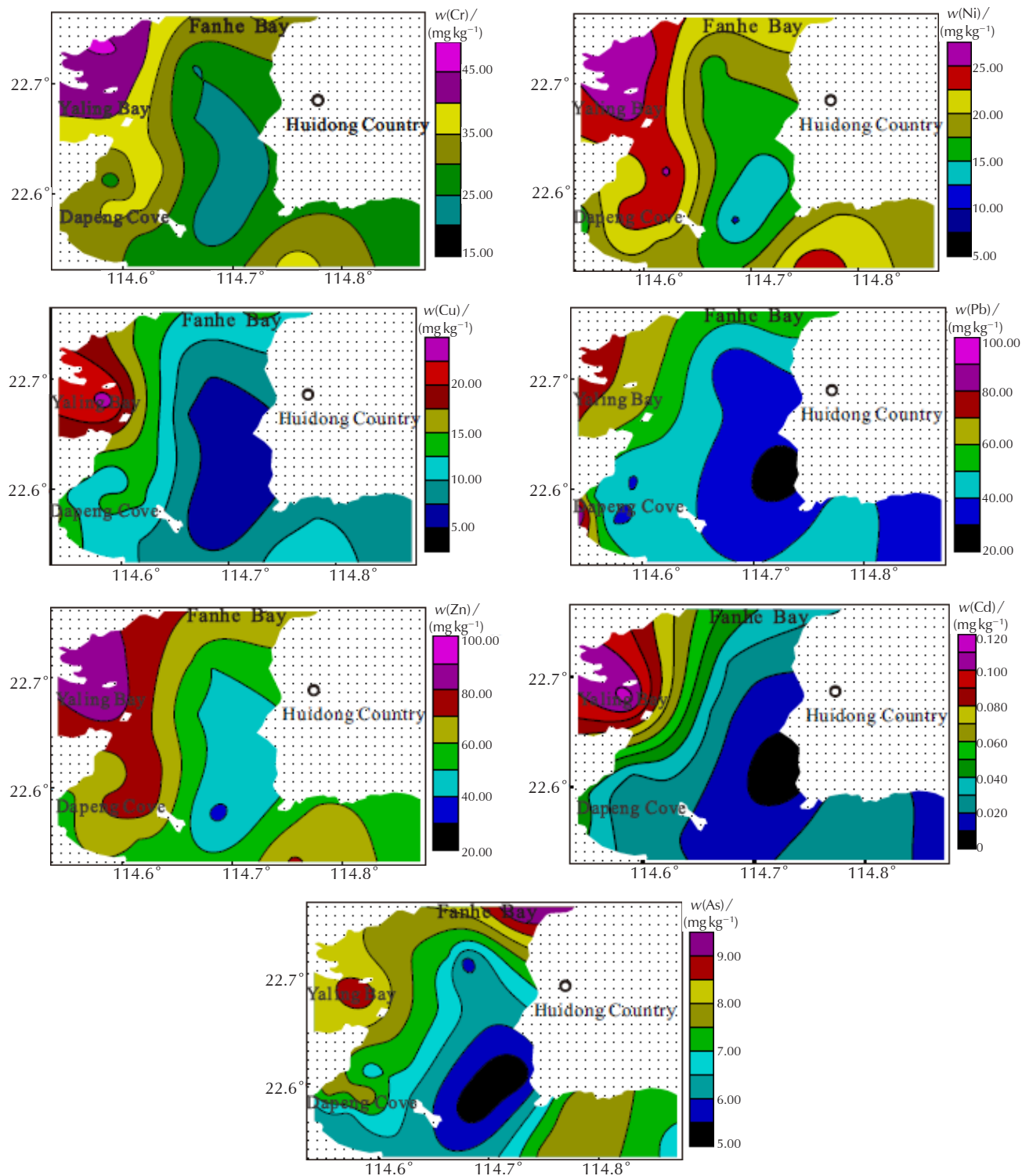


Fig. 2 – Spatial distribution of selected elements concentrations in surface sediments  
Slika 2 – Prostorne varijacije koncentracija odabranih elemenata u površinskom sedimentu

70.2 % and 11.3 %, respectively. Of all the sampled sediments, only Z07 and Z11 near Dapeng Cove were sandy silt, Z13 was medium sand. Overall, the distribution of granularity in Daya Bay was more uniform.

The distribution of the selected elements in the studied region displayed large spatial variations (Fig. 2), and showed

a ring shape and descending trend from the shore to the bay by varying degrees in accordance with the results of previous studies.<sup>10</sup> The relatively high content of Ni, Cu, Pb, Zn, Cd and As occurred in the Dapeng Cove, Fanhe Bay and Yaling Bay. The highest values for Cu, Pb, Zn, Ni and Cd were found near Dapeng Cove and Yaling Bay, while the maximum zone for As was in Fanhe Bay. All met-

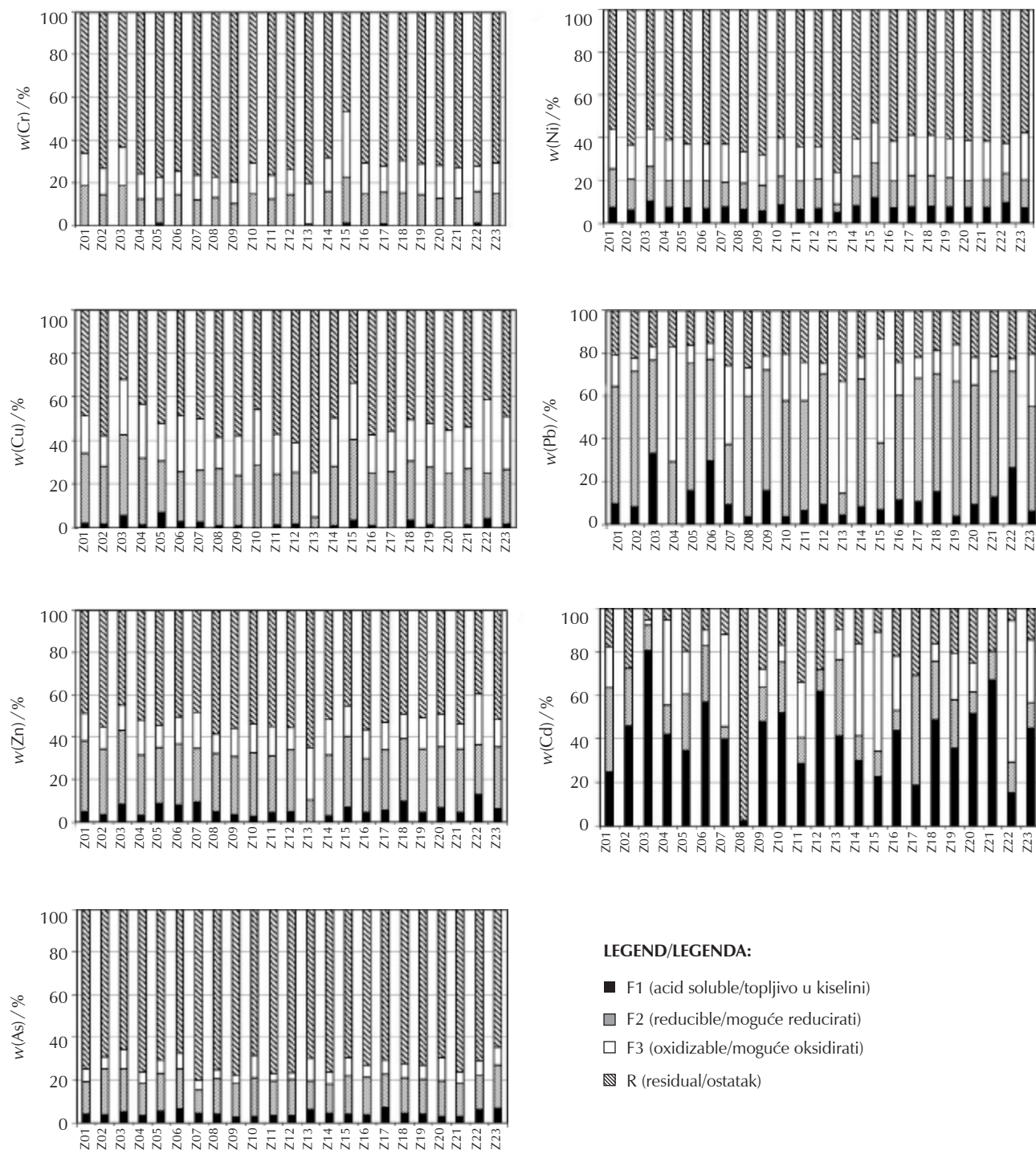


Fig. 3 – Distribution of heavy metals in different fractions in Daya Bay surface sediments  
Slika 3 – Raspodjela teških metala u frakcijama površinskog sedimenta u zaljevu Daya

als reached a maximum value at Z05 located in an aquaculture area and near the densely polluted coastal region in Yaling Bay. The causes of the observed distribution are unknown. However, it is reasonable to propose that the human activity in the tested area contributed significantly to the enrichment of these metals in DYB. Other than three small rivers discharging into Dapeng Cove, there are no large rivers discharging into DYB. The organic matter content (TOC) in the Daya Bay surface sediments varied slightly with values ranging from 0.58 % – 1.10 % and an average value of 0.78 %. The spatial distribution pattern of TOC was in accordance with the distribution of the selected metals tested.

### Heavy metal speciation distributions

As shown in Fig. 3, Cr, Ni, Cu, Zn, As, and Mn and Fe were found associated mainly with the residual fraction (R), while Pb was predominantly bound to reducible fraction (F2). In contrast, the majority of Cd was preferentially localized in the acid-soluble fraction (F1), indicating that this fraction was the main form for Cd to migrate from liquid to solid phase, which was in accordance with the result of Lin.<sup>3</sup> The selected metals bound to exchangeable fractions in F1 through absorption to humus and clay minerals, which are sensitive to changes in the environment, can easily migrate and transform, and have high bioavailability and toxicity. The selected metals bound to carbonates in F1 through co-precipitation with carbonate minerals and are released easily under acidic conditions. The F2 fraction is the part of the metals wrapped by Fe/Mn oxide or hydroxide precipitation, which is difficult to release due to strong ionic bonding. In the F3 fraction, the selected metals are combined with organic matter reactive groups or generate water-insoluble material with sulphur ions, so they are not easily released under normal moderate reduction or a weak oxidizing environment. The metals bound to R fraction are mainly incorporated within the crystal lattices of silicates, and can only be released during weathering processes, so they are not considered bioavailable because the weathering process is much longer than the life period.<sup>11</sup> Therefore, the ranking order of migration and transformation on the basis of the non-residual content of the metals was Pb > Cd > Cu > Zn > Ni > Cr > As in Daya Bay surface sediments.

### Biological assessment

It has been well established that the release of heavy metals and bioavailability are higher with the increasing percentage of the non-residual (F1 + F2 + F3) fractions of the sediments.<sup>12</sup> In classical geochemistry, the primary and secondary phases are referred to as the primary minerals and the secondary metabolites in F1, F2 and F3 fractions, respectively. Since heavy metals from manmade pollution sources are in the secondary phase, the extent of heavy metal pollution in sediments could be evaluated with the ratio of secondary to primary phases ( $K_{RSP}$ ). According to previous studies,  $K_{RSP} < 1$ ,  $1 < K_{RSP} < 2$ ,  $2 < K_{RSP} < 3$ , and  $K_{RSP} > 3$ , indicate no pollution, light pollution, moderate pollution, and heavy pollution, respectively. The  $K_{RSP}$  of the selected metals were in the following descending order: Cd > Pb > Cu > 1 > Zn > Ni > Cr > As. The average  $K_{RSP}$

value of Cd was 9.34, while the average value of  $K_{RSP}$  for Pb was 4.93, suggesting that the studied sediments are heavily polluted with Cd and Pb. The mean  $K_{RSP}$  values of Cu and Zn were 1.01 and 0.95, respectively. However, the  $K_{RSP}$  values of Zn were greater than 1 in eight sampling stations. These results indicate that the studied sediments are only slightly polluted with Cu and Zn. The  $K_{RSP}$  values of As, Cr and Ni were less than 1, indicating that there was basically no pollution in this area for As, Cr and Ni.

### Correlations

The correlation analysis was carried out to determine the relationships between the sediment characteristics (TOC, clay, Mz, Mn-F2 and Fe-F2)<sup>†</sup> and the extracted heavy metals of each fraction by IBM SPSS 19.0. As shown in Table 1 (\*\* $p < 0.01$  and \* $p < 0.05$ ), the analysis results were as follows.

(1) The F2 and total fraction of Cr, Ni and Zn were significantly correlated with TOC, Mn-F2, Fe-F2, clay and silt. For Cr, the F1 fraction was correlated with clay and silt, and F3 with TOC. The R fraction showed positive correlation with TOC ( $r = 0.730$ ,  $p < 0.01$ ), clay ( $r = 0.361$ ,  $p < 0.05$ ) and silt, respectively. For Ni, the F1 and F3 fraction showed significant correlation with TOC and silt, while R with TOC ( $r = 0.807$ ,  $p < 0.01$ ), clay ( $r = 0.350$ ,  $p < 0.05$ ) and silt ( $r = 0.510$ ,  $p < 0.05$ ). Moreover, the F1 and F3 of Zn were correlated with silt and TOC separately, and R with TOC ( $r = 0.866$ ,  $p < 0.01$ ), clay ( $r = 0.367$ ,  $p < 0.05$ ) and silt ( $r = 0.512$ ,  $p < 0.05$ ). So TOC, clay and silt mainly affected the distribution of Cr, Ni and Zn because the main fraction of Cr, Ni and Zn was R in this area.

(2) The total Cu was significantly correlated with TOC, Mn-F2 and Fe-F2 at  $p < 0.01$ . The F2 fraction was correlated with TOC, Mn-F2 and Fe-F2. The F3 and R fractions were correlated with TOC. In this area, the R fraction was the main speciation of Cu, so Cu was mainly influenced by TOC. In addition, the main factors influencing As was also TOC.

(3) The F2 and total fraction of Pb were found significantly correlated with TOC, Mn-F2, Fe-F2 and silt. For the other three fractions, only the Pb in R fraction was correlated with TOC at  $p < 0.01$ . Therefore, the main factors influencing Pb in DYB were Fe-F2, TOC, silt, Mn-F2 and clay because Pb was mainly bound to F2 fraction.

(4) For Cd, the total and F1 showed significant correlation with TOC, the correlation coefficients being 0.464 ( $p < 0.05$ ). The Cd in residual fraction was correlated with TOC ( $r = 0.494$ ,  $p < 0.05$ ), and silt ( $r = 0.497$ ,  $p < 0.05$ ). Therefore, TOC mainly affected the distribution of Cd because the main fraction of Cd was F1 in this area.

### Principal Component Analysis (PCA)

To analyse further the general characteristics of the sediments in the studied region, the multivariate Principal Component Analysis (PCA) were conducted. PCA analysis incorporates the seven metal concentration data of all

<sup>†</sup> The data Mn-F2 and Fe-F2 refer to reference 10.

Table 1 – Correlation between fractions and environmental factors

Tablica 1 – Korelacija između frakcija i okolišnih čimbenika

Total Ukupno	Cr-total Ukupno Cr	Ni-total Ukupno Ni	Cu-total Ukupno Cu	Pb-total Ukupno Pb	Zn-total Ukupno Zn	Cd-total Ukupno Cd	As-total Ukupno As
TOC	0.864**	0.871**	0.766**	0.569**	0.870**	0.225	0.579**
Mn-F2	0.782**	0.870**	0.682**	0.363*	0.858**	0.257	0.719**
Fe-F2	0.823**	0.918**	0.629**	0.440*	0.874**	0.161	0.460
clay/glina	0.375*	0.369*	0.145	0.327	0.360*	-0.016	-0.156
silt/mulj	0.475*	0.567**	0.339	0.387*	0.562**	0.101	0.002
F1	Cr-F1	Ni-F1	Cu-F1	Pb-F1	Zn-F1	Cd-F1	As-F1
TOC	0.242	0.864**	0.238	0.171	0.192	0.464*	-0.352*
clay/glina	0.434*	0.312	0.121	0.146	0.209	0.133	-0.364*
silt/mulj	0.527**	0.522*	0.172	0.177	0.373*	0.117	-0.369*
F2	Cr-F2	Ni-F2	Cu-F2	Pb-F2	Zn-F2	Cd-F2	As-F2
TOC	0.766**	0.818**	0.682**	0.711**	0.861**	0.025	0.694**
Mn-F2	0.621**	0.839**	0.572**	0.665**	0.836**	0.196	0.796**
Fe-F2	0.740**	0.933**	0.564**	0.768**	0.880**	0.094	0.587**
clay/glina	0.369*	0.356*	0.214	0.378*	0.391*	-0.197	0.047
silt/mulj	0.579**	0.638**	0.347	0.673**	0.604**	-0.007	0.204
F3	Cr-F3	Ni-F3	Cu-F3	Pb-F3	Zn-F3	Cd-F3	As-F3
TOC	0.708**	0.869**	0.557**	0.164	0.522*	-0.216	0.435*
clay/glina	0.136	0.362*	0.079	0.122	0.020	-0.152	-0.283
silt/mulj	0.196	0.545**	0.221	-0.024	0.205	-0.018	-0.325
R	Cr-R	Ni-R	Cu-R	Pb-R	Zn-R	Cd-R	As-R
TOC	0.730**	0.807**	0.855**	0.625**	0.866**	0.494*	0.480*
clay/glina	0.361*	0.350*	0.072	0.204	0.367*	0.161	-0.116
silt/mulj	0.417*	0.510*	0.335	0.341	0.512*	0.497*	0.054

sampling stations and explores the possible similar distribution behaviour of metals. In our study, the two principal components (PCs) extracted together explained 71.10 % (PC1: 48.58 %; PC2: 22.52 %) of the metal variance. The principal component analysis loading plot (Fig. 4) showed that these metals were classified into Group 1 (Cr, Ni, Cu, Pb and As) and Group 2 (Cd and Zn) according to similarities in the behaviour and distribution of these metals in the sediments. Firstly, all five metals in group 1 were strongly associated with PC1 (positive loading). Notably, Cu, Cr, As and Ni were mainly present in R fraction, reflecting lithogenic origin. Thus, PC1 is supposed to reflect the contribution of natural geological sources of metals in the coastal sediments. With regard to Group 2, the PCA results showed that Cd and Zn diverged significantly and were mainly present in F1 and R fraction, respectively. The research results<sup>5,7</sup> show that industrial wastewater often contains large amounts of metals. The Daya Bay includes a large area of farming land, and the contribution to the high proportion of Cd in F1 and F2 might mainly be related to cage culture activities (feeding fodder) and fishing boats. Therefore, PC2 might represent industrial wastewater and aquacultural activity factor.

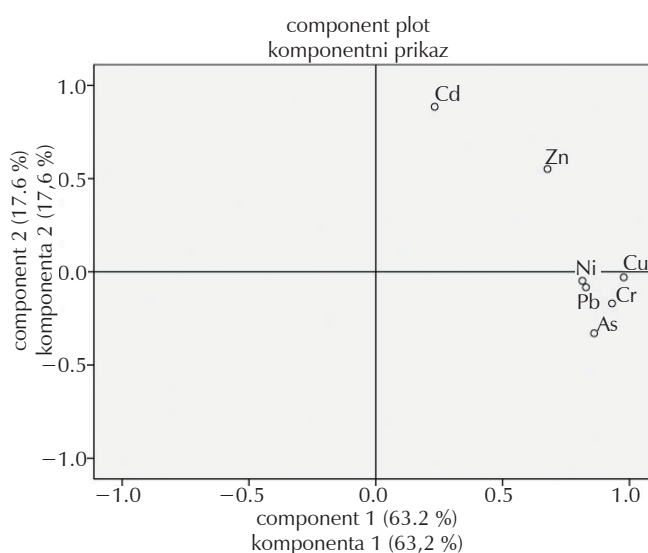


Fig. 4 – Principal component analysis loading plot of metallic elements

Slika 4 – Analiza glavnih komponenata učitanja podataka metalnih elemenata

## Conclusions

In the present study, chemical analysis and speciation of Cr, Cu, Ni, Zn, Pb, As and Cd between acid-soluble (F1), reducible (F2), oxidizable (F3) and residual (R) fractions were investigated in the contaminated sediments from the Daya Bay. The studied region has been negatively impacted by different anthropogenic activities as indicated by high contents of selected metals, such as Cd, Cu, Pb and Zn. Furthermore, the combination of high concentrations of Cd, Cu, Pb and Zn, and high percentage of association to the non-residual fraction (F1 + F2 + F3) has raised serious concerns in terms of the necessity for adequate strategies during dredging activities. TOC was the most important factor influencing the selected metals in Daya Bay as determined by the Pearson correlation analysis. The results of this study indicate the necessity of further studies for a better understanding of the feasibility of recovering different metals, and the technologies that can be applied in a cost-effective manner.

## Conflict of interest

We have no conflict of interest to declare.

## ACKNOWLEDGEMENTS

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## List of symbols and abbreviations

### Popis simbola i kratica

DYB	– Daya Bay – zaljev Daya
BCR	– Community Bureau of Reference – Ured za standardizaciju Europske Zajednice
PCA	– principal components analysis – analiza glavnih komponenata
ICP-MS	– inductively coupled plasma-mass spectrometry – induktivno povezana spektrometrija plazma-masa
F1	– fraction 1 (acid soluble fraction) – frakcija 1 (topljivo u kiselini)
F2	– fraction 2 (reducible fraction) – frakcija 2 (moguće reducirati)
F3	– fraction 3 (oxidizable fraction) – frakcija 3 (moguće oksidirati)
F4	– R (residual fraction) – R (frakcija ostatka)
TOC	– total organic carbon – ukupni organski ugljik
GBW	– offshore marine sediment – morski sediment u blizini obale
$K_{RSP}$	– the ratio of secondary to primary phases – omjer sekundarnih i primarnih faza

Mz	– mean grain size – srednja veličina zrna
w	– mass fraction, % – maseni udjel, %

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## SAŽETAK

### Frakcioniranje toksičnih metala i polumetala u sedimentima zaljeva Daya u Južnokineskom moru

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Profili metala u sedimentima zaljeva Daya (DYB) u Kini određeni su sekvencijskom ekstrakcijom prema proceduri koju je izradio *European Community Bureau of Reference*. Da bi se odredili pokretljivost i biodostupnost otrovnih metala (Cr, Cu, Ni, Zn, Pb i Cd) i polumetala (As), 2011. godine prikupljeni su i analizirani uzorci površinskog sedimenta s 23 reprezentativne lokacije. Pronađen je sljedeći redoslijed migracija, transformacija te stupnja zagađenja: Pb > Cd > Cu > Zn > Ni > Cr > As. Smatra se da među tim elementima olovo predstavlja ozbiljnu prijetnju za ljudsko zdravlje i okoliš zbog znatnog udjela nereziđualnih oblika. Omjer primarne i sekundarne faze pokazuje da su proučavani sedimenti umjereno do jako onečišćeni bakrom i cinkom, također kadmijem i olovom. Povezanost varijabli (metala i polumetala) na svakom koraku uzastopnih ekstrakcija procijenjena je multivarijatnom analizom, uključujući i korelacijsku analizu i analizu glavnih komponenata. Zahvaljujući tim analizama, utvrđen je moguć izvor zagađenja. Korelacijska analiza pokazala je da je sadržaj ukupnog organskog ugljika najvažniji faktor koji utječe na raspodjelu otrovnih elemenata u zaljevu Daya. Analiza glavnih komponenata (PCA) pokazala je da proučavani elementi u području DYB-a potječu uglavnom od prirodnog trošenja stijena, potom i iz industrijskih otpadnih voda i otpadnih voda akvakulture.

#### Ključne riječi

Toksični elementi, frakcioniranje metala, sekvencijska ekstrakcija, procjena rizika, sediment, zaljev Daya

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