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# TOTAL CONTENTS AND SEQUENTIAL EXTRACTIONS OF HEAVY METALS IN BANG PAKONG RIVER ESTUARINE SEDIMENTS

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## ABSTRACT

*Samples of sediments collected along the Bang Pakong River were analysed for Cu, Pb, Zn, Cd, Cr and Ni contents by atomic absorption spectrometry. Determinations of redox potential, organic carbon, hydrogen sulfide, and grain size analysis were also performed. The sequential extractions revealed that high percentages of Cr, Ni, and Cu are associated/transported in the residual fraction, thus being practically impossible to release to the environment on the deteriorating scale. In contrast, Pb, Zn, and Cd were found mostly associated/transported in the leachable fractions which can be remobilized and released to the environment by various physical-chemical processes. Hence the selective distribution of trace metals should be taken into account and caution must be exercised in evaluation of risk of potential release of these metals in the environment.*

## INTRODUCTION

Presently, the role of heavy metals as pollutants is widely recognized[1,2,3,4,5,6]. Some elements, notably copper, cadmium, lead and zinc, have at times been found in high concentrations in the marine environment, apparently in relation to naturally occurring deposits[1,6,7]. Anthropogenic activities, however, still remain the cause of the increased amount of heavy metals which have been dumped into oceans. For this reason, the analysis of metals in sediments can be quite helpful in detecting sources of pollution in the aquatic system. However, most of the works reported sediments analyses in term of total metal concentrations. Knowledge of the total amount of metal alone is not sufficient to indicate the risk of toxicity or even to understand the various geochemical processes[8,9] because non-residual metals have the potential to become environmentally mobile and ready bioavailable whereas residual metals are nearly unbioavailable. Therefore use of total concentrations as a criterion to assess the potential effects of sediment contamination implies that all forms of a given metal have an equal impact on the environment, such an assumption is clearly untenable. Since the distribution of trace metals in various chemical fractions is important in evaluating the more readily available forms of metals that are associated with sediments, several extraction procedures with chemical solutions have been developed[10,11,12]. However, all of these have some limitations and their use as analytical tools is controversial[13]. The main problems include the non-selectivity of extractants and a possible trace element redistribution among phases during extraction. Despite this, the leaching techniques still represent one of the few tools available for examining trace metal associations in sediments.

In the present study, distribution of Cu, Pb, Zn, Cd, Cr, and Ni were studied in an operationally defined extraction scheme. The functionally defined sediment phases investigated included the *exchangeable, oxidizable, carbonate, reducible and residual phase*. Among the various procedures of sequential extraction reported in the literature, Tessier's method[12] and later modified by Meguellati *et al.*[14] was adopted. In addition, the determination of Eh, organic carbon, $H_2S$, and grain-size analysis were also performed. Atomic absorption spectrophotometry was employed in the metal determinations.

## MATERIAL AND METHODS

### Sample collection and treatment

The sampling location for the sediment samples are shown in Figure1. Typical depth core samples were obtained using PVC tubes. The tubes were immediately sealed at both ends with plastic sheets. The cores were then sectioned by plastic knife under nitrogen atmosphere at 3-cm intervals up to a depth of 10 cm and at 5-cm below that depth. The pH and Eh of the sediment sections were determined by direct insertion of a glass electrode and a platinum electrode respectively into the sediment cores. The titration method given by Gaudette *et al.* [15] was used for the determination of organic carbon in sediments.

The sediment sections were dried overnight at 110 degree celcius, ground and homogenized with an agate mortar, and sieve through a nylon sieved (2 mm mesh size) to eliminate coarse fragments before proceeding to the sequential extractions.

### sequential extractions and total metals analysis

According to the method proposed by Meguellati *et al.*[14], five metal fractions were obtained: 1. exchangeable phase; 2. oxidizable phase(organic fraction and sulphides); 3. carbonate phase; 4. reducible phase(Fe and Mn oxyhydrates); and 5. residual phase. The following extraction were employed for extraction of metals from chemical phases in sediments.

Step 1 : exchangeable phase: 1M $BaCl_2$, 16 ml, 2 hrs shaking.

Step 2 : oxidizable phase : 30% $H_2O_2$ + 0.02 M $HNO_3$ (5V +3V), 16 ml, 5 hrs shaking + 1 hr 98 °C, extracted with 3.5 M $CH_3COONH_4$,10 ml, 1 hr shaking.

Step 3 : carbonate phase : 1M $CH_3COOH$ + 0.6 M $CH_3COONa$, 35 ml, 5 hrs shaking.

Step 4 : reducible phase : 0.1 M $NH_2OH\,HCl$ + 25%(v/v) $CH_3COOH$, 35 ml, 4 hrs shaking + 1 hr 98°C, extracted with 3.5 M $CH_3COONH_4$, 10 ml, 1 hr shaking.

Step 5 : residual phase : Conc. HF-$HClO_4$ (5V+V), 12 ml 100-150°C evaporated to dryness conc $HClO_4$, 2 ml, 100-150°C evaporated to dryness and conc. $HNO_3$ 2 ml, 60-80°C, 15-30 min.

Metals in each leaching solutions were then determined by atomic absorption spectrophotometry ( Hitachi 180-30). For the trace metals Cu, Pb, Zn, Cd, Cr and Ni, a standard addition technique was employed because of matrix effects, presumably due to material leached from the sediments, were observed; these effects would have contributed in many cases to an error of as much as 10%.

For total metals analysis, the solid was digest using the same method as the digestion for residual phase (step5). The resulting solution was then analyzed by atomic absorption spectrophotometry for trace metals using standard addition technique.

### Data quality tests

The analytical precision for each of the extraction steps, and for the overall procedure, was tested by subjecting two sub-sediment samples to sequential procedure described above; the results obtained are shown in Table1. Comparison of the sum of the metal concentrations in the individual fractions with the total metal concentration shows good agreement for all trace metals. A standard reference material for trace metals ( MESS-1) from the National Research Council, Canada was used to check the accuracy of the analysis, the results obtained are shown in Table 2.

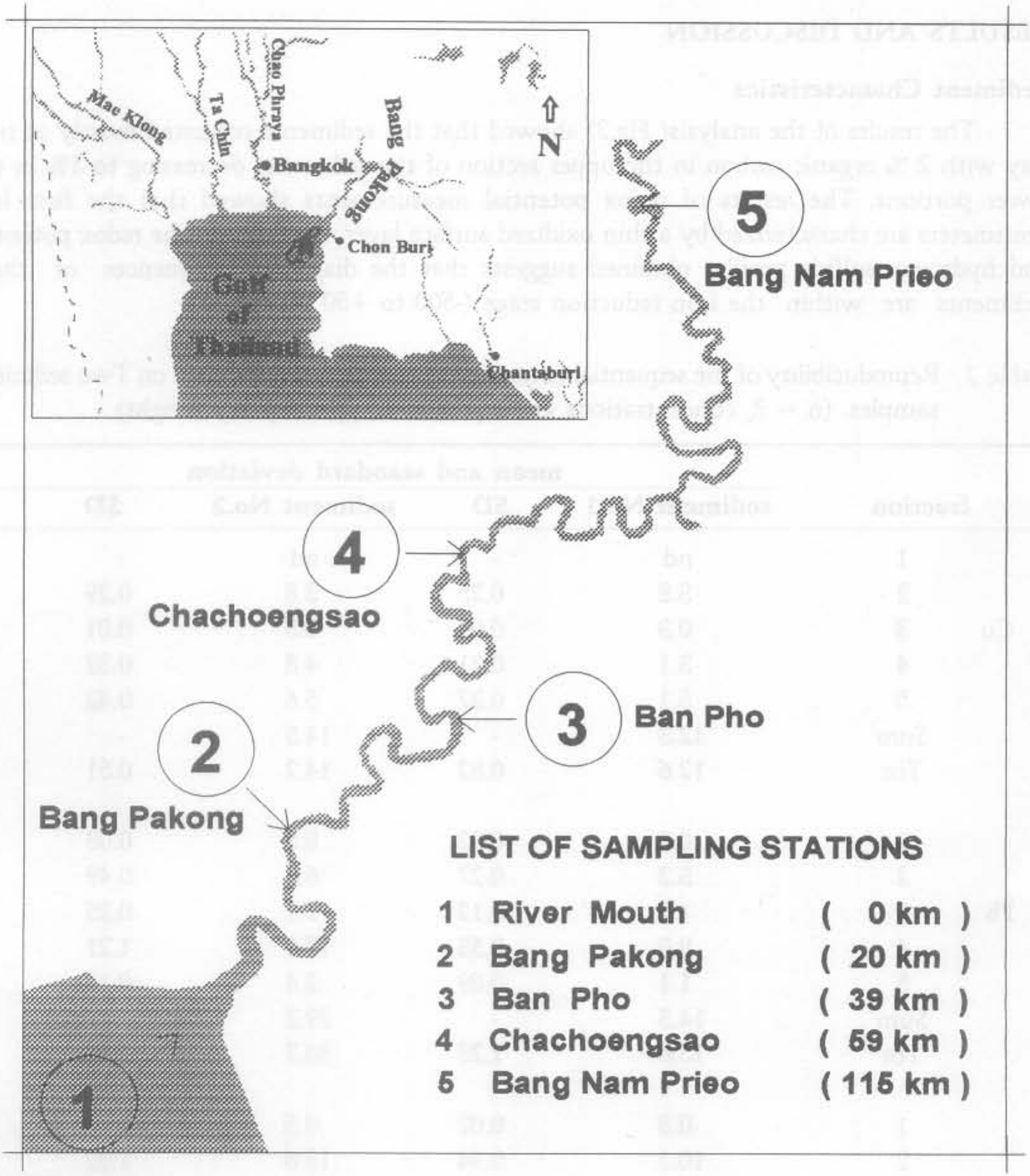

**Fig.1** Sampling stations along the Bang Pakong River.

## RESULTS AND DISCUSSION

### Sediment Characteristics

The results of the analysis( Fig.2) showed that the sediments consisted mostly of silty clay with 2 % organic carbon in the upper section of the sediments decreasing to 1% in the lower portions. The results of redox potential measurements showed that the first few centimeters are characterized by a thin oxidized surface layer. In addition, the redox potential and hydrogen sulfide profiles obtained suggests that the diagenetic sequences of these sediments are within the iron reduction stage (-500 to +50 mv)[16].

Table 1. Reproducibility of the sequential extraction procedure as determined on Two sediment samples. (n = 3, concentrations are expressed in ppm. by dry weight)

| | | **mean and standard deviation** | | | |
|---|---|---|---|---|---|
| **fraction** | | **sediment No.1** | **SD** | **sediment No.2** | **SD** |
| Cu | 1 | nd | - | nd | - |
| | 2 | 3.8 | 0.25 | 3.8 | 0.29 |
| | 3 | 0.3 | 0.01 | 0.3 | 0.01 |
| | 4 | 3.1 | 0.21 | 4.8 | 0.32 |
| | 5 | 5.1 | 0.37 | 5.6 | 0.42 |
| | Sum | 12.3 | - | 14.5 | - |
| | Tot | 12.6 | 0.82 | 14.2 | 0.51 |
| Pb | 1 | 0.3 | 0.02 | 0.5 | 0.03 |
| | 2 | 3.2 | 0.27 | 6.2 | 0.49 |
| | 3 | 1.7 | 0.12 | 3.1 | 0.25 |
| | 4 | 8.0 | 0.53 | 17.0 | 1.21 |
| | 5 | 1.1 | 0.09 | 2.4 | 0.13 |
| | Sum | 14.3 | - | 29.2 | - |
| | Tot | 15.6 | 1.23 | 30.2 | 2.12 |
| Zn | 1 | 0.3 | 0.02 | 0.5 | 0.03 |
| | 2 | 10.2 | 0.94 | 13.6 | 1.02 |
| | 3 | 6.9 | 0.37 | 9.1 | 0.42 |
| | 4 | 14.1 | 1.12 | 18.4 | 1.27 |
| | 5 | 4.5 | 0.32 | 5.1 | 0.37 |
| | Sum | 36.0 | - | 46.7 | - |
| | Tot | 34.5 | 1.65 | 45.6 | 2.59 |
| Cd | 1 | nd | - | nd | - |
| | 2 | 0.13 | 0.01 | 0.14 | 0.01 |
| | 3 | 0.02 | - | 0.02 | - |
| | 4 | 0.14 | 0.01 | 0.15 | 0.01 |
| | 5 | 0.03 | - | 0.04 | - |
| | Sum | 0.32 | - | 0.35 | - |
| | Tot | 0.40 | 0.03 | 0.46 | 0.03 |

Table 1. (Cont'd)

| | fraction | mean and standard deviation | | | |
|---|---|---|---|---|---|
| | | **sediment No.1** | **SD** | **sediment No.2** | **SD** |
| | 1 | 0.8 | 0.05 | 0.9 | 0.07 |
| | 2 | 1.5 | 0.12 | 1.6 | 0.14 |
| Cr | 3 | 1.4 | 0.09 | 1.6 | 0.12 |
| | 4 | 1.4 | 0.13 | 1.4 | 0.10 |
| | 5 | 7.2 | 0.53 | 8.4 | 0.72 |
| | Sum | 12.3 | - | 13.9 | - |
| | Tot | 13.1 | 1.09 | 14.4 | 0.95 |
| | 1 | 0.7 | 0.04 | 0.8 | 0.05 |
| | 2 | 2.3 | 0.12 | 2.6 | 0.19 |
| Ni | 3 | 1.6 | 0.11 | 1.8 | 0.15 |
| | 4 | 2.3 | 0.19 | 2.8 | 0.21 |
| | 5 | 6.9 | 0.54 | 6.4 | 0.52 |
| | Sum | 13.8 | - | 14.4 | - |
| | Tot | 14.9 | 0.68 | 15.8 | 0.86 |

Sum = represents the sum of the five fractions

Tot = represents the total metal concentration

fraction 1 = exchangeable phase, fraction 2 = oxidizable phase,

fraction 3 = carbonate phase, fraction 4 = reducible phase,

fraction 5 = residual phase.

Table 2. Analysis of reference material (MESS-1). All units in ppm.

| **Element** | **Certified value** | **This study (n=6)** | **% recovery** | **C.V.*** |
|---|---|---|---|---|
| Zn | 191±17 | 199.5±11 | 104.5 | 5.51 |
| Cr | 71±11 | 59.2±4 | 83.4 | 6.76 |
| Cu | 25.1±3.8 | 21.3±1.2 | 84.9 | 5.63 |
| Pb | 34.0±6.1 | 29.9±2.6 | 87.9 | 8.69 |
| Cd | 0.59±0.10 | 0.45±0.05 | 76.3 | 11.11 |
| Ni | 29.5±2.7 | 26.0±2.0 | 88.1 | 7.69 |

* C.V. = Coefficient of variation.

## Sequential Extraction Results

The results of the analysis which compiled in Table 3 and Figure 3 present the average values of Cu, Pb, Zn, Cd, Cr, and Ni found in Bang Pakong River sediments as a percentage of the total extracted by the sequential extraction procedures. A detailed examination of the analysis revealed that most of the Cr (60%) transported in the Bang Pakong River sediments is carried in the crystalline particles of the sediments (residual fraction). To the lesser extent, most of the Ni (44.2%) and Cu (40.1%) are also associated with the residual fraction. Thus residual phase is found to be the primary important transport phase for Cr, Ni, and Cu. Similar results were reported for Cr, Ni,and Cu in the Amazon and the Yukon rivers as reported by Gibbs[17] . This similarlity is particularly interesting since the three rivers are in extremely different climates and since these three rivers are believed to be unpolluted rivers.

Those Cr which incorporated into solid biological material(oxidizable phase,11.9%) , carbonate mineral (carbonate phase,11.3%),and coprecipitation in metallic coating ( reducible phase,10.7%) are found to be the second, third, and fourth major transport phases for Cr. While reducible phase and oxidizable phase are the second and third major transport phases for Ni and Cu respectively. Since most of these elements (40.1-60.0%) are found to be associated with the residual phase or locked in the alumino-silicate lattice of the sediments thus being practically impossible to release to the environment on the deteriorating scale.

Table 3 Percentage of total amounts of Cd, Pb, Zn, Cd, Cr, and Ni associated with five different transport/chemical fractions in Bang Pakong River

| Transport/chemical fraction | Cu | Pb | Zn | Cd | Cr | Ni |
|---|---|---|---|---|---|---|
| 1. Exchangeable | - | 1.7 | 0.9 | - | 6.2 | 5.0 |
| 2. Oxidizable | 24.5 | 20.8 | 31.1 | 37.3 | 11.9 | 18.1 |
| 3. Carbonate | 1.9 | 10.6 | 19.8 | 6.7 | 11.3 | 13.6 |
| 4. Reducible | 33.5 | 58.3 | 36.8 | 47.5 | 10.7 | 19.1 |
| 5. Residual | 40.1 | 8.6 | 11.4 | 8.6 | 60.0 | 44.2 |

In contrast to Cr, Ni, and Cu as described above, Pb, Zn, and Cd were found mostly associated with leachable fractions such as reducible, oxidizable, and carbonate phases. Among these transport phases, reducible phase(36.8-58.3%) is the primary important transport phase whereas, oxidizable(20.8-37.3%) and carbonate phases(6.7-19.8%) are second and third major transport phases for Pb, Zn, and Cd. These leachable fractions can be remobilized and released to the environment by various processes such as changing in the ionic force, Eh(redox potential), or pH and etc. Therefore, any physical-chemical modification of the nature might bring about considerable metal concentrations in the environment. Since these metals can be remobilized and released to the environment as described, hence, caution must be exercised in evaluation of risk of potential release of these metals in the environment.

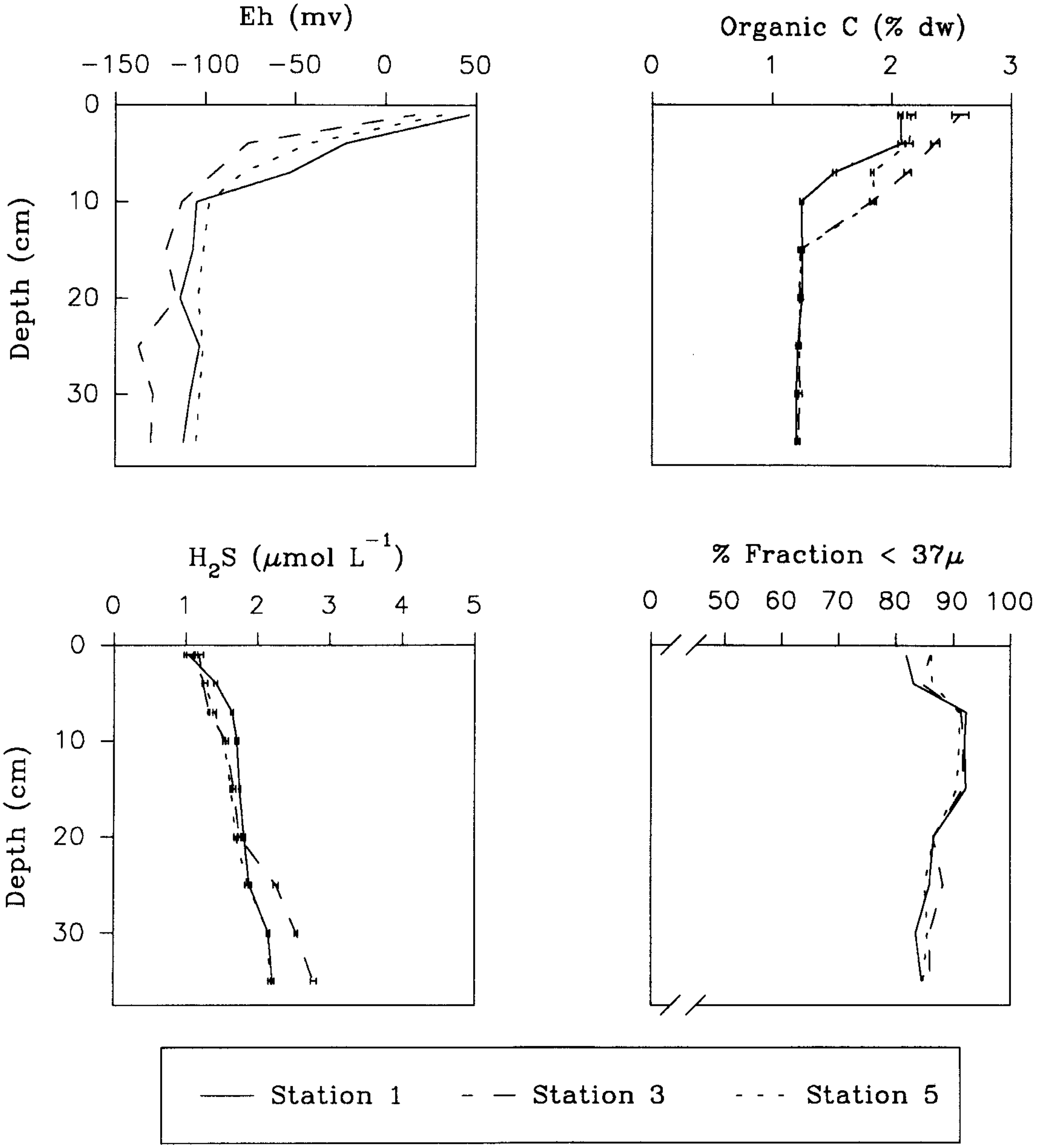

**Fig.2** Profiles of Eh, organic carbon, hydrogen sulfide, and percentage of sediment < 37 mm at stations 1, 3, and 5 of the Bang Pakong River Estuary sediments.

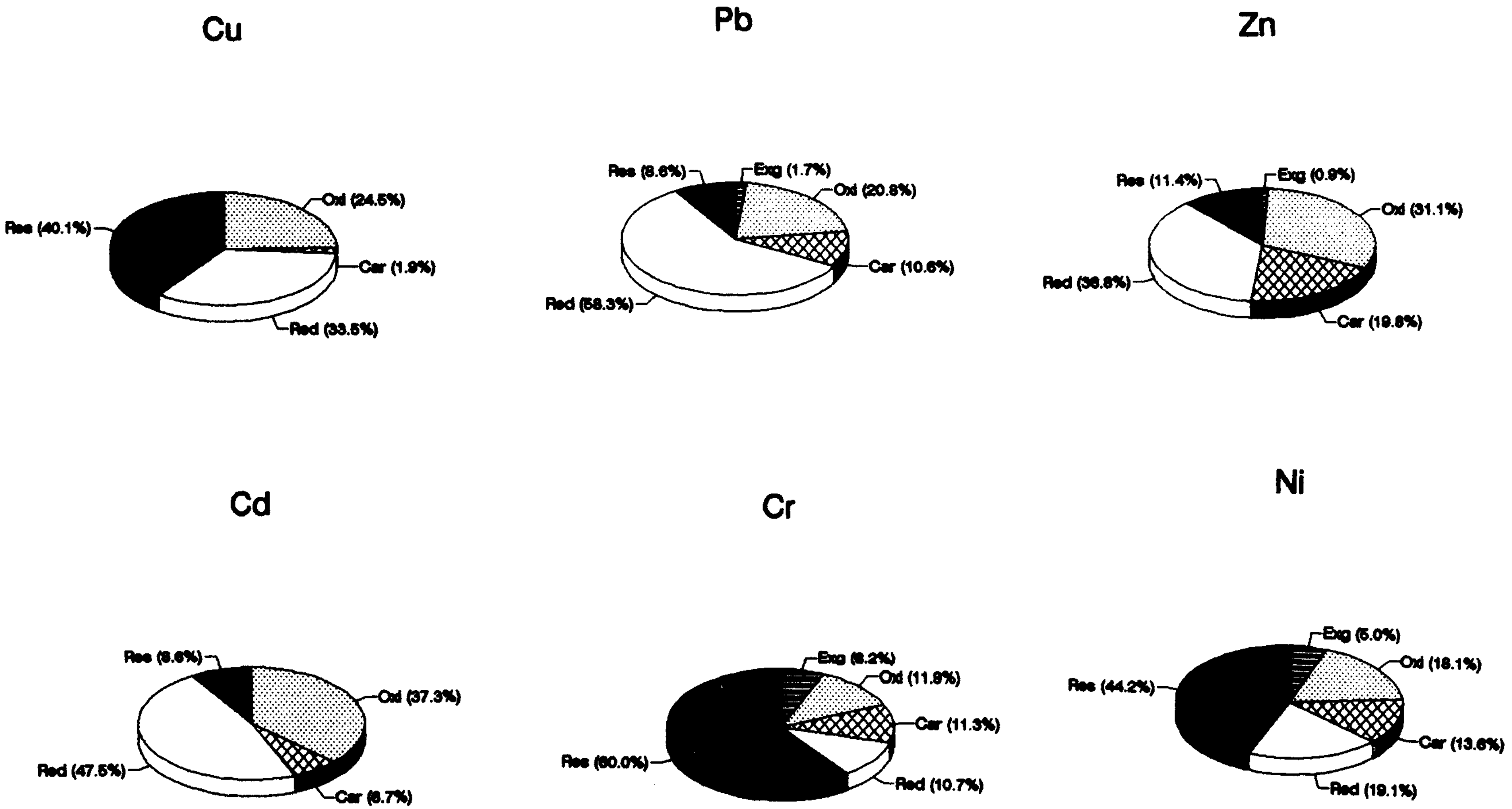

**Fig.3** The average values of Cu, Pb, Zn, Cd, Cr, and Ni found in Bang Pakong River sediments as a percentage of the total extracted by the selective extraction procedures.

The results of the study indicated that transportation of trace metals in exchangeable phase accounts for a non-significant percentage of the total contents for most elements except in the case of Cr and Ni which found to be about 5.0-6.2%. This is probably due to the high affinity of Cr and Ni to the clay minerals found in the riverine sediments. However, the available data are not sufficient to provide an adequate description. Further investigation is still needed.

Figure 4-6 show the vertical distribution of six heavy metals ( Cr, Ni, Cu, Pb, Zn, and Cd ) in stations 1,3 and 5 in five sequential extraction steps. The largest portion of sediment Cr, Ni, and Cu were found in the residual phase. Sediment Cr and Ni in the most abundant fraction(residual fraction) were the most uniform, showing no significant difference between sites or depths within sites, whereas a significant decrease with depth occurred in case of Cu, Pb, Zn and Cd.

The sequential chemical extraction data for Pb, Zn, and Cd indicated greater differences in fractional distribution for Pb, Zn, and Cd than for Cr, Ni and Cu ( Fig.4-6). The largest portion of Pb,Zn, and Cd were found in the reducible fraction and showed no significant difference between sites. However, significant decrease with depth of Pb, Zn, and Cd in the reducible fraction were seen. It is possible that Pb, Zn, and Cd which were found mostly associated with the reducible fraction ( Fe/Mn oxides) may have been remobilized from depths in relation to iron and manganese recycling (under the reducing environment as evidenced by decreased Eh and increased hydrogen sulfide concentrations in the Bang Pakong sedimentary column, see Fig. 2). Mobilization of reducible Fe/Mn has been shown to occur rapidly with decreased redox potential in the deeper portions of the sediment core as described by Chester[18] Loss of Fe/Mn oxides from the deeper sections of the Bang Pakong River sediments, therefore results in the decrease of the concentration of those metals bound with Fe/Mn oxides in the sedimentary column.

## CONCLUSION

It can be concluded that Cr, Ni, and Cu in the Bang Pakong River sediments are mostly transported in the residual fraction or carried in the crystalline particles of the sediments, thus being difficult to release to the environment on the deteriorating scale. In contrast Pb, Zn, and Cd were found mostly associated with the leachable fractions such as reducible, oxidizable and carbonate phase. This implies that Pb, Zn, and Cd can be remobilized and released to the environment by various physical-chemical processes. The results of the study also showed significant decrease with depth of Pb, Zn, and Cd in the reducible fraction. This is probably due to the remobilization of Fe/Mn oxides in the deeper sections of the Bang Pakong River sedimentary column.

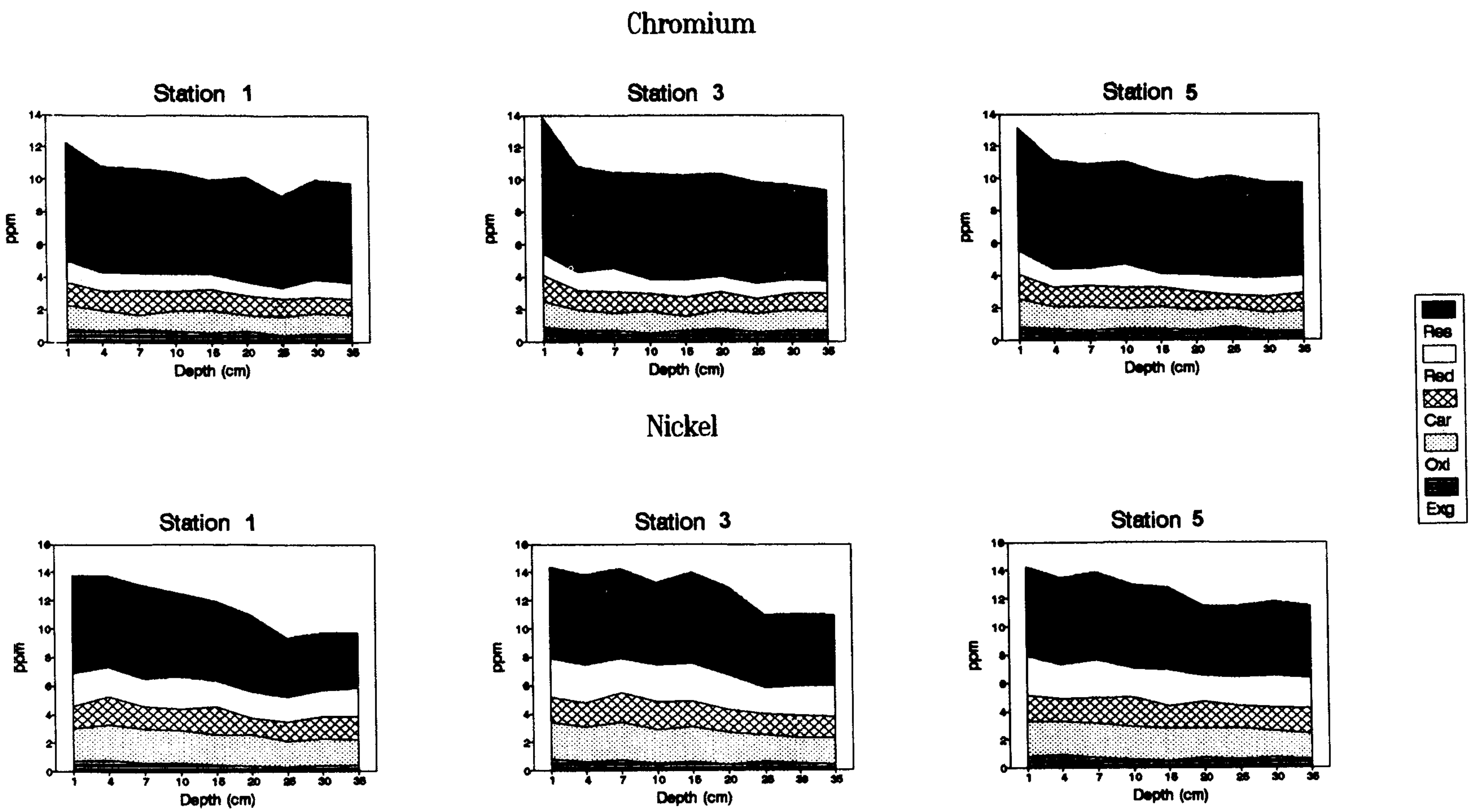

**Fig.4** Distribution of Chromium and Nickel in stations 1,3 and 5 in five sequential extraction steps. ( Res = residual phase, Red = reducible phase, Car = carbonate phase, Oxi = Oxidizable phase, Exg = exchangeable phase.)

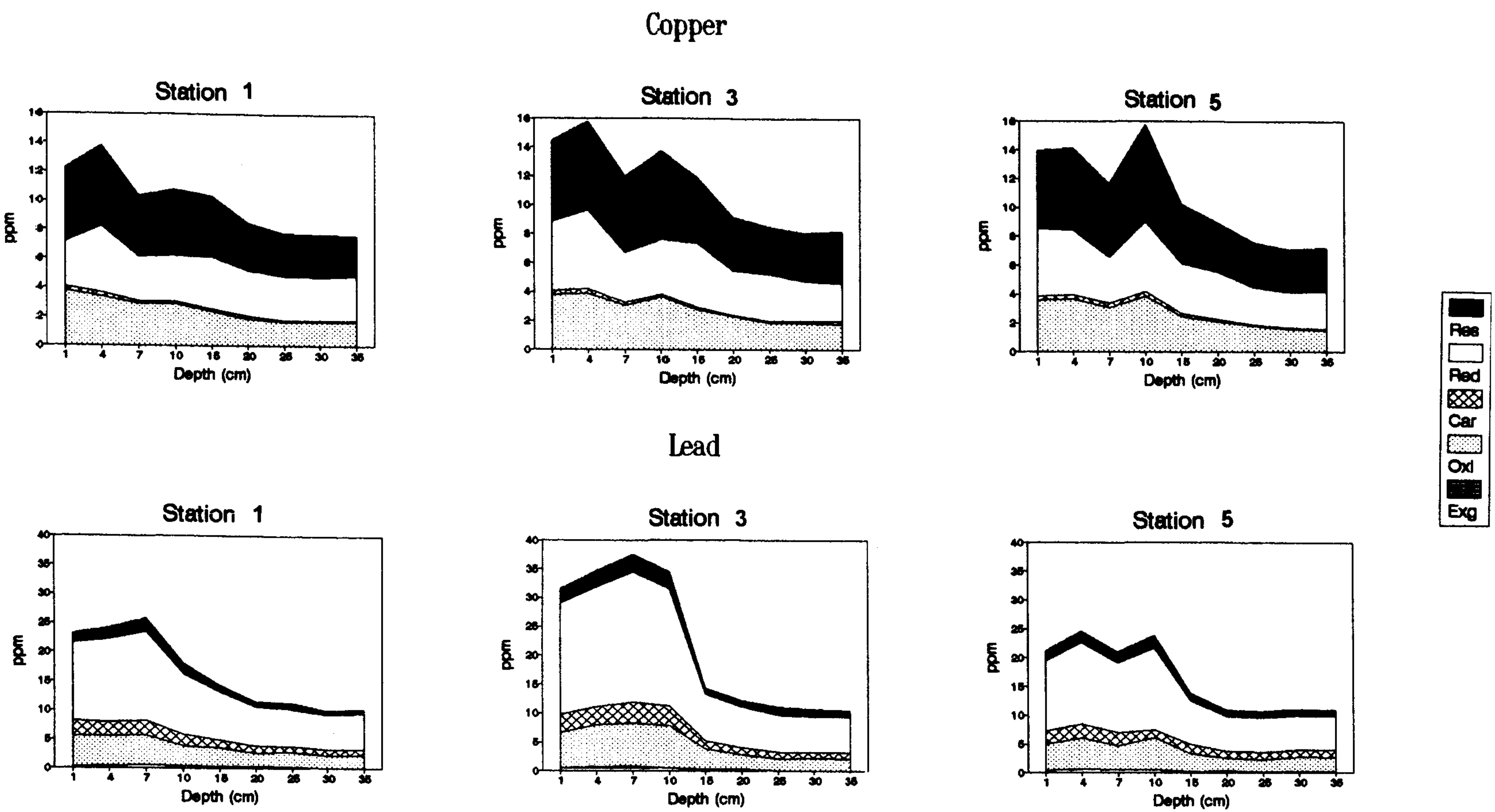

**Fig.5** Distribution of Copper and Lead in stations 1,3 and 5 in five sequential extraction steps. ( Res = residual phase, Red = reducible phase, Car = carbonate phase, Oxi = Oxidizable phase, Exg = exchangeable phase.)

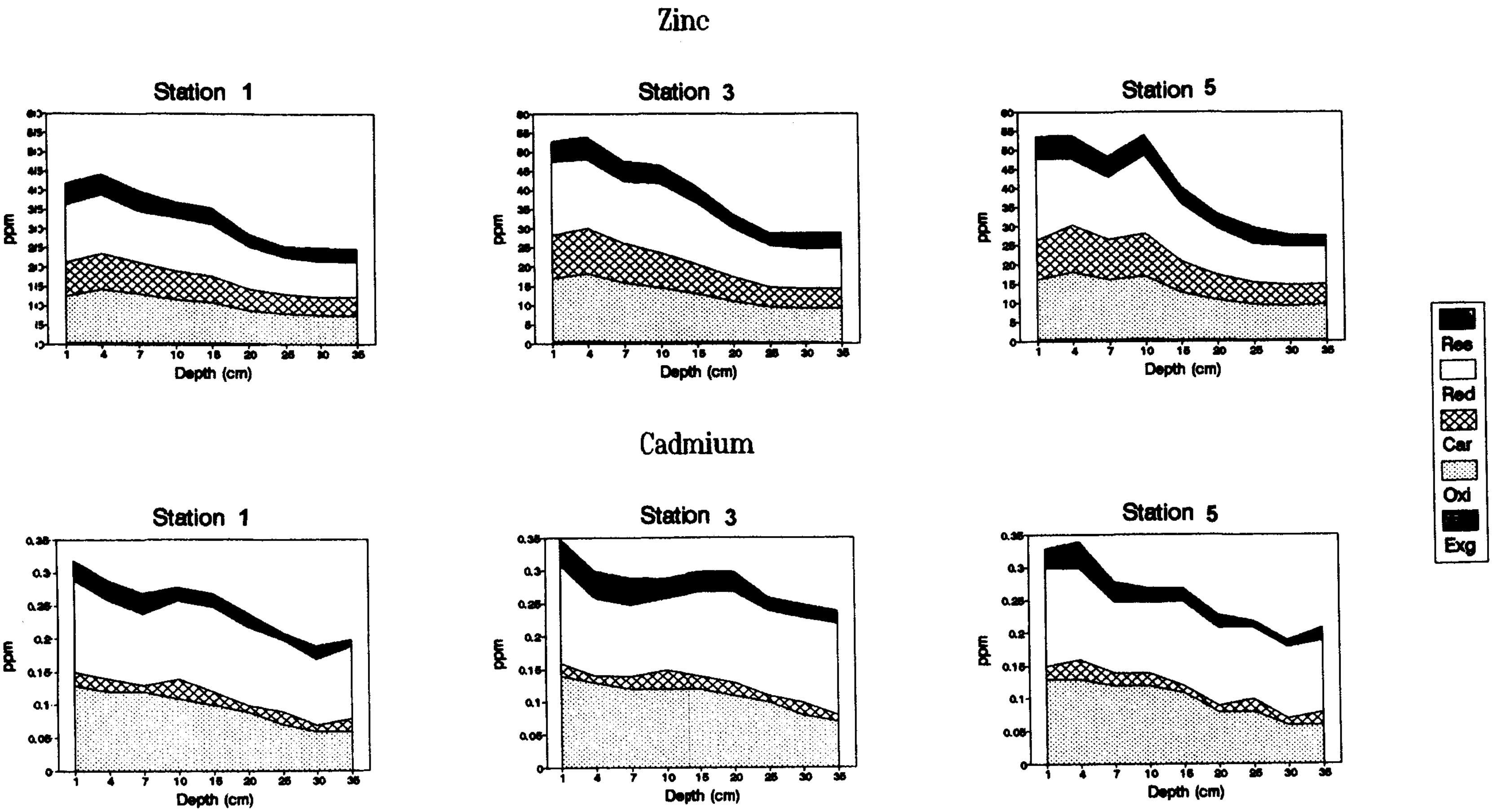

**Fig.6** Distribution of Zinc and Cadmium in stations 1,3 and 5 in five sequential extraction steps. ( Res = residual phase, Red = reducible phase, Car = carbonate phase, Oxi = Oxidizable phase, Exg = exchangeable phase.)

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## บทคัดย่อ

ได้เก็บตัวอย่างดินตะกอนจากปากแม่น้ำบางปะกงเพื่อทำการวิเคราะห์หาปริมาณของ ทองแดง ตะกั่ว สังกะสี แคดเมี่ยม โครเมี่ยม และ นิเกิล โดยวิธีอะตอมมิกแอปซอฟชั่น สเปกโตรโฟโตเมตรี และยังได้ทำการวิเคราะห์หาค่ารีดอกโพแทนเชียน คาร์บอนอินทรีย์ ไฮโดรเจนซัลไฟด์ เพื่อเป็นข้อมูลเสริม. นอกจากนี้ได้ใช้วิธีสกัดแยกตามลำดับส่วน เพื่อหาปริมาณของโลหะที่สะสมอยู่ในส่วนประกอบต่างๆทางเคมี และหรือรูปแบบการขนถ่ายโลหะปริมาณน้อยในดินตะกอน. ผลการศึกษาพบว่า ส่วนใหญ่ของโครเมียม นิเกิล และทองแดงจะถูกสะสมและขนถ่ายในรูปของเรซิดวล ( residual phase ) ซึ่งโลหะจะถูกกักอยู่ในผลึกอะลูมิโนซิลิเกต ของดินตะกอน และยากต่อการถูกชะล้างและปลดปล่อยออกสู่สิ่งแวดล้อมในระดับที่จะเป็นอันตราย. ตรงกันข้าม ตะกั่ว สังกะสี และแคดเมียม ถูกสะสมและขนถ่ายในรูปแบบที่สามารถถูกชะล้างออกสู่สิ่งแวดล้อมได้ ( leachable fraction ตัวอย่างเช่นใน exchangeable, oxidizable, carbonate, และ reducible phase เป็นต้น ) โดยการเปลี่ยนแปลงของสภาพแวดล้อมทั้งทางกายภาพและเคมี. ดังนั้นการกระจายของปริมาณโลหะหนักในรูปแบบต่างๆจึงมีความสำคัญ และควรถูกนำมาพิจารณาอย่างระมัดระวังในการประเมินผลความเสี่ยงอันเนื่องมาจากการปลดปล่อยของสารโลหะหนักในดินตะกอนสู่สิ่งแวดล้อม.