

Distribution of Trace Metals in Sediments of Mokpo Coastal Area after a Strong Rainfall

Do Hee Kim* and Yong Sik Sin

Department of Ocean System Engineering, Mokpo Maritime University,
Mokpo 530-729, Korea

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The characteristics of trace metals were investigated in the sediments of the Mokpo coastal area, southwestern coast of Korea. Surface sediments were collected in September 3, 2002 after a strong rain event. The sampling sites were categorized into the inner and outer harbour based on salinity distribution and difference of trace metal concentration was evidence between these two zones. The enrichment factor (E·F) of Zn and Cr were high at the mouth of Mokpo Harbour and E·F of Cu was high at the east-south of Dali Island. One hundred percent of Mn and Pb samples and 40% of Zn samples had E·F higher than 1 suggesting that they are accumulated in the entire outer of Mokpo Harbour. Trace metals appeared to be accumulated in the inner harbour by input of sediments in the discharged freshwater from Young-San River during strong rainfall whereas they were influenced by natural sedimentation and human activities in part.

Key words: Mokpo coastal area, Sediments, Rainfall, Trace metal

Introduction

Marine sediments are ultimate sinks for particulate materials supplied to the oceans by rivers and the atmosphere (Yeats and Bowers, 1983). The trace metals flow into coastal and they are transferred to sediments through adsorption onto suspended matter and subsequent sedimentation (Hart, 1982). The surface layer of sediments can be assumed to be in a state of equilibrium with the overlying water column. Sediment bound trace metals may, therefore, become a source of pollution to the water column (Zwolsman et al., 1996).

In urbanized regions these materials are often influenced by domestic, industrial and mining activities leading to increased trace metal concentrations (Bruland et al., 1974; Duinker and Nolting, 1976, 1977; Martin and Whitfield, 1983; Martin et al., 1989). A large portion of the metal enriched particles are deposited and buried in the coastal sediments. When these sediments remain more or less undisturbed,

they can provide us with an historical pollution record (Bruland et al., 1974; Bertine, 1980; Macdonald et al., 1991; Nolting and Helder, 1991). Marine sediments are used to investigate anthropogenic influences on marine environment.

Trace metal concentrations in estuaries sediments have been widely reported for regulatory and management purposes (Fracers, 1993; Garbarinom et al., 1995; Lee et al., 1998) and for defining spatial and temporal distributions (French, 1993; Cundy et al., 1997; Bothner et al., 1998). Studies of trace metals in sediments of Korea were to focused on local concentrations and factors controlling concentrations (Cho et al., 1994; Hong et al., 1983; Song et al., 1997; Shim et al., 1998; Youn et al., 1999).

The Mokpo Harbour had littoral transport for long periods over one hundred years and has constructed cement barriers, Young-San embankment, Young-Am embankment and Keum-Ho embankment for drainage since 1981. The patterns of sedimentation and trace metal accumulated in the Mokpo Harbour may be different from those in other estuaries due to high discharge rates of freshwater

*Corresponding author: doking@mail.mmu.ac.kr

from the embankments during the rain season.

The objective of the present study was to investigate the characteristics of trace metal concentrations and contamination processes of the trace metals in sediments of the Mokpo coastal area after a strong rainfall using enrichment factor and residual analysis.

Materials and Methods

Analysis of trace metal in sediments is generally based on two methods; total digestion method and extracted method. Total digestion method uses strong acid to dissolve all the trace metals in sediments, but it is difficult to identify effects on environments since acids dissolve the components not related to environmental factors. Extracted method was used in this study since the experimental procedure is simple and potential effects on marine environment can be identified (Ministry of Maritime Affairs and Fisheries of Korea, 1998).

The sediment core samples were collected with a cylindrical corer (i.d=5 cm) using the Mokpo Maritime University Research vessel 706 at 25 stations (Fig. 1) on September 3, 2002. Rainfalls recorded 76% of total yearly rainfalls from July to September in Mokpo coastal regions. The cylindrical corer was designed to obtain undisturbed sediments and was closed during sampling to prevent contamination.

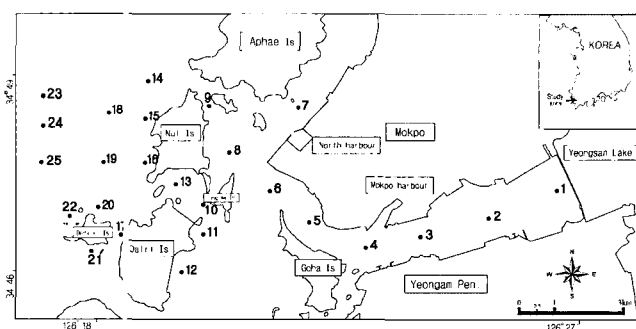


Fig. 1. Maps showing the sampling station.

The sediment core samples were cut in slices of 5 cm thickness from the surface of the sampled sediments. The sediment samples were transferred to polypropylene bottle and stored at -20°C until analysis. Approximately 5 g of each slice was dried at 60°C and 200 mg was transferred into a 10 mL centrifuge test tube which was filled with 10 mL of

1 N HNO_3 solution, and the sediment was extracted at room temperature for 1 hr with continuous agitation and centrifuged 4,000 rpm for 10 minutes. Fe, Mn, Zn, Cu, Pb, and Cr were analyzed in the supernatant on sediment by the air-acetylene flame atomic absorption spectrophotometer with an instrument of model Shimadzu AA-6701F (Ministry of Maritime Affairs and Fisheries of Korea, 1998).

The analysis detection limits for the trace metal in sediments were as follows; 0.004 mg/kg dry for Cu, 0.003 mg/kg dry for Cd, 0.580 mg/kg dry for Pb, 0.001 mg/kg dry for Zn and 0.008 mg/kg dry for Fe. The contents of trace metals were calculated using the standard addition method. Certified Reference Material NIES CRM No. 12 (National Institute for Environmental Studies, Japan Environmental Agency) were analyzed with approximately every 7 samples to assess accuracy and precision. The range of the recoveries of metals studied were from 69% to 90%. It is low recovery rate, since the content of trace metal was extracted from sediment by nitric acid.

The samples for IL and sediment composition were also analyzed contemporary and salinity was measured according to the manual presented by Ministry of Maritime Affairs and Fisheries of Korea (1998). Statistical analysis of data was performed with Excel program.

Distribution and accumulation of trace metals are mainly controlled by grain size of sediments. Gradients of contaminant concentration and regional difference can be determined not by pollution but by sediment grain size. For that reason, we study on the particles size smaller than $63\ \mu\text{m}$ are criteria in this study.

Enrichment Factor (E·F) was employed as the criteria for natural level of trace metal concentration in the sediments of sampling sites. Enrichment factor defined as a ratio of trace metals and conservative elements in sample to those in average shale from Equation (1) represents the factor where Fe is used as conservative (Horowitz, 1991). Trace metal concentrations surpass natural level when the factor is higher than 1.

$$E \cdot F = \frac{[C_{\text{metal}}/C_{\text{Fe}}]_{\text{sample}}}{[C_{\text{metal}}/C_{\text{Fe}}]_{\text{average shale}}} \quad (1)$$

In order to determine contamination of trace metal in sediments, concentrations of trace metal in se-

diments were normalized based on Fe for sediment grain size. Residual analysis of linear regression was used to investigate effects of contamination and spatial distributions.

Results and Discussion

The rainfall recorded 384 mm for August 2002 (Mokpo Wether Center, 2002) and freshwater flow to the Mokpo Harbour from the Young-San River was higher than other season. Table 1 presents results on the sediment trace metals, IL and grain size ($<63 \mu\text{m}$), salinity collected from the Mokpo Harbour regions in September 3, 2002 when freshwater input was high (27,838,000 tons).

Table 1. Results of salinity, sediment grain size and extracted trace metals in sediments of the Mokpo coastal area

| Station | Trace metals (mg/kg dry) | | | | | | IL % | $<63 \mu\text{m}$ % | Salinity ‰ |
|---------|--------------------------|-----|------|-----|------|------|------|---------------------|------------|
| | Fe | Mn | Zn | Cu | Pb | Cr | | | |
| 1 | 5,466 | 161 | 43.9 | 9.1 | 13.4 | 8.68 | 9.5 | 52.1 | 7.7 |
| 2 | 5,721 | 223 | 65.4 | 9.5 | 14.2 | 4.51 | 8.2 | 52.4 | 6.9 |
| 3 | 3,960 | 202 | 32.1 | 9.5 | 10.2 | 5.74 | 6.5 | 53.0 | 5.9 |
| 4 | 3,355 | 275 | 23.4 | 9.7 | 8.0 | 3.49 | 5.9 | 56.6 | 6.7 |
| 5 | 3,073 | 247 | 22.5 | 5.4 | 8.6 | 5.44 | 6.4 | 55.4 | 7.9 |
| 6 | 2,454 | 327 | 82.2 | 3.7 | 8.5 | 7.95 | 4.6 | 67.1 | 10.7 |
| 7 | 3,270 | 283 | 24.2 | 3.6 | 9.2 | 4.10 | 5.2 | 77.5 | 14.3 |
| 8 | 1,465 | 239 | 27.4 | 1.6 | 7.6 | 1.89 | 2.4 | 23.2 | 15.7 |
| 9 | 3,007 | 217 | 48.2 | 4.4 | 5.3 | 8.33 | 5.5 | 90.3 | 17.7 |
| 10 | 3,265 | 237 | 19.3 | 5.7 | 9.8 | 5.17 | 5.4 | 95.0 | 18.0 |
| 11 | 3,087 | 215 | 84.9 | 4.1 | 7.6 | 5.06 | 5.5 | 96.8 | 15.4 |
| 12 | 3,254 | 331 | 21.6 | 3.5 | 5.7 | 1.88 | 6.0 | 98.0 | 14.3 |
| 13 | 3,422 | 352 | 76.1 | 5.3 | 9.7 | 3.31 | 6.4 | 98.7 | 17.3 |
| 14 | 2,456 | 238 | 16.9 | 2.6 | 5.6 | 1.87 | 10.4 | 70.4 | 14.8 |
| 15 | 2,962 | 259 | 50.7 | 3.1 | 6.6 | 1.56 | 5.3 | 93.7 | 25.5 |
| 16 | 2,796 | 224 | 19.4 | 6.9 | 10.1 | 1.77 | 5.6 | 97.8 | 25.3 |
| 17 | 3,699 | 425 | 28.4 | 5.1 | 8.4 | 2.40 | 6.7 | 98.8 | 19.4 |
| 18 | 3,046 | 349 | 18.0 | 2.9 | 6.7 | 1.15 | 5.9 | 76.2 | 21.0 |
| 19 | 2,646 | 306 | 20.1 | 5.8 | 7.7 | 0.84 | 4.9 | 67.3 | 21.4 |
| 20 | 3,553 | 386 | 46.5 | 6.3 | 8.1 | 4.84 | 6.5 | 99.5 | 21.0 |
| 21 | 3,457 | 338 | 20.2 | 4.3 | 5.0 | 2.23 | 6.9 | 99.5 | 19.6 |
| 22 | 3,072 | 288 | 22.6 | 3.8 | 5.2 | 5.24 | 5.4 | 97.7 | 19.1 |
| 23 | 2,928 | 254 | 23.3 | 3.5 | 5.9 | 7.34 | 5.7 | 90.7 | 20.6 |
| 24 | 2,874 | 220 | 21.2 | 3.8 | 5.4 | 4.29 | 5.1 | 75.2 | 21.9 |
| 25 | 2,579 | 224 | 40.9 | 3.7 | 3.1 | 7.27 | 4.2 | 56.4 | 21.9 |

Concentration differences of Fe, Cu and Pb were shown between the inner and outer harbour whereas differences of other trace metals were not evident. Salinity ranged from 5.9 to 7.9 ‰ in the inner harbour station 1 to 5. Whereas from 10.7 to 25.5 ‰ in

the outer harbour station 6 to 25 (Fig. 2). Based on average and standard deviations of salinities, we present and discuss results from the sampling sites categorized into the inner and outer harbour.

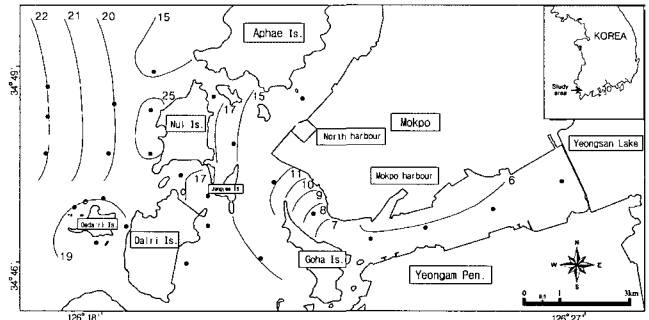


Fig. 2. Profile of salinity in Mokpo coastal area after a strong rainfall in Sept. 3, 2002.

Distribution of trace metals in sediments is affected by grain size of sediments since it determines rates of trace metals ions absorption and ion-exchange in sediment (Horowitz, 1991). In general, correlation exists between grain size of sediments and content of conservative elements (Al, Fe and Mn) and organic matter. Conservative elements are therefore used to remove effect of sediment grain size.

Contents of particles smaller than $63 \mu\text{m}$ increased in downstream in the inner harbour whereas contents of trace metals and IL decreased in downstream. Contents of small particles ($<63 \mu\text{m}$) and trace metal-IL were negatively correlated (Table 2).

Table 2. Relationship between the content of trace metal and sediment composition, IL in inner coastal area

| | $63 \mu\text{m} >$ | Fe | Mn | Zn | Cu | Pb | Cr | IL |
|--------------------|--------------------|-------|-------|------|-------|------|------|----|
| $63 \mu\text{m} >$ | 1 | | | | | | | |
| Fe | -0.86 | 1 | | | | | | |
| Mn | 0.89 | -0.68 | 1 | | | | | |
| Zn | -0.76 | 0.93 | -0.44 | 1 | | | | |
| Cu | -0.35 | 0.51 | -0.24 | 0.43 | 1 | | | |
| Pb | -0.90 | 0.99 | -0.71 | 0.94 | 0.39 | 1 | | |
| Cr | -0.64 | 0.44 | -0.91 | 0.15 | -0.07 | 0.48 | 1 | |
| IL | -0.81 | 0.89 | -0.83 | 0.70 | 0.23 | 0.89 | 0.77 | 1 |

Percentage of particles smaller than $63 \mu\text{m}$ was minimum (23%) at station 8 where river flow is high and maximum (99.5%) at station 20, 21 near the Oedalri Island. Station in the inner harbour had lower percentage (over 50%) than expected. At

station 1 and 2 concentrations of Pb and Cr were high and concentrations of Zn and Cu were high at station 11. Mn and IL were high at station 13 and 14. Concentration Fe, Cu, IL were minimum at station 8 mouth of the Mokpo Harbour where flow rates were high and contents of small particles in the sediment were low. Mn had minimum concentration at station 1.

This result suggests that the trace metals were not accumulated by natural sedimentation over long-term but by short-term that deposition due to fresh water inputs during the wet season. This hypothesis is supported by result that the contents small particles were low (50%) at station 1 to 5 whereas contents were high at other stations in outer harbour. On the other hand, the correlations of Fe with Zn, Pb and IL is evidence and the accumulation of the metals may be controlled by same mechanisms.

In the outer harbour, the contents of small particles (<63 μm) ranged from 67.1 to 99.5% (mean 83.9%) in the sediments of the harbour. The correlation between contents of small particles and Fe was evident ($r=0.88$) as reported in Table 3 unlike in the inner harbour. Difference correlations of Fe and grain size between the inner and outer harbour may be due to freshwater inputs into the inner harbour whereas accumulated in the outer harbour for a long time. The element of Fe was used as conservative to calculate E·F. E·F can be used to investigate anthropogenic effect since contents of the trace metal in sediments increase when anthropogenic input are introduced (Horowitz, 1991; Cho et al., 1994).

Table 3. Relationship between the content of trace metal and sediment composition, IL in outer coastal area

| | 63 μm > | Fe | Mn | Zn | Cu | Pb | Cr | IL |
|--------------------|--------------------|------|-------|-------|-------|-------|-------|----|
| 63 μm > | 1 | | | | | | | |
| Fe | 0.88 | 1 | | | | | | |
| Mn | 0.30 | 0.53 | 1 | | | | | |
| Zn | 0.10 | 0.04 | 0.05 | 1 | | | | |
| Cu | 0.27 | 0.17 | -0.21 | 0.52 | 1 | | | |
| Pb | 0.17 | 0.16 | 0.24 | 0.21 | 0.17 | 1 | | |
| Cr | 0.04 | 0.01 | -0.28 | 0.43 | 0.11 | -0.21 | 1 | |
| IL | 0.48 | 0.43 | 0.24 | -0.16 | -0.01 | -0.06 | -0.23 | 1 |

In this study, we calculated E·F of trace metal in the sediments based on content of trace metals in terrestrial sediments (Martin and Whitfield, 1983)

and assumed that trace metals were introduced by anthropogenic inputs when E·F is higher than 1.

The E·F of Zn and Cr were high at the mouth of Mokpo Harbour station 6 and decreased in downstream. The E·F of Cu was high at the south-east of Dali Island and decreased in downstream. One hundred percent of Mn and Pb samples and 40% of Zn samples had E·F higher than 1 suggesting that they are accumulated in the entire outer of Mokpo Harbour. Thirty percents of Cr samples showed that Cr was accumulated especially at the northern west region of Mokpo Harbour. Ten percents of Cu samples had E·F higher than 1 especially at the south east of the Dali Island. Maximum E·F of Mn, Zn, Cu, Pb and Cr was 4.54, 2.99, 4.66, 8.13 and 1.88, respectively showing 8 times high in the sediment of some regions (Fig. 3).

Effects of grain size were normalized by dividing trace metal concentrations by Fe concentrations. Spatial variations (standard deviation/mean) in ratio of trace metal concentration to Fe concentration were 110.1%, 64.8%, 62.5% and 23.3% for Cu, Cr, Zn and Mn respectively. Spatial distributions of Mn/Fe and Pb/Fe concentrations showed that the contents of the metals were high in the North Harbour where small-scaled ship yards are located and in the region between the Mokpo Harbour mouth (Koha Island) and open ocean whereas they were low in other regions. This suggests than the trace metals are introduced from the North Harbour by local rain effects.

Contaminated sediments were identified by residual analysis of linear regression together with E·F. In the residual analysis, conservation elements and grain size were used for regression to investigate effects of contamination and spatial distributions. Regress analysis is simple but outlier can affect the relationship between two parameters.

To minimize the effects, absolute values of residuals were used and contents of small particle (<63 μm) and Fe were used to represent grain size since correlation of two components was high ($r=0.88$). Samples with higher residual standard deviation (SD) than mean SD of absolute residuals were selected to distinguish high residuals from residuals in the regression. Those exceed 95% probability in the total samples. Residuals exceeding 1.96 SD for Mn, Zn, Cu, Pb and Cr were 104.1 mg/kg dry, 43.6

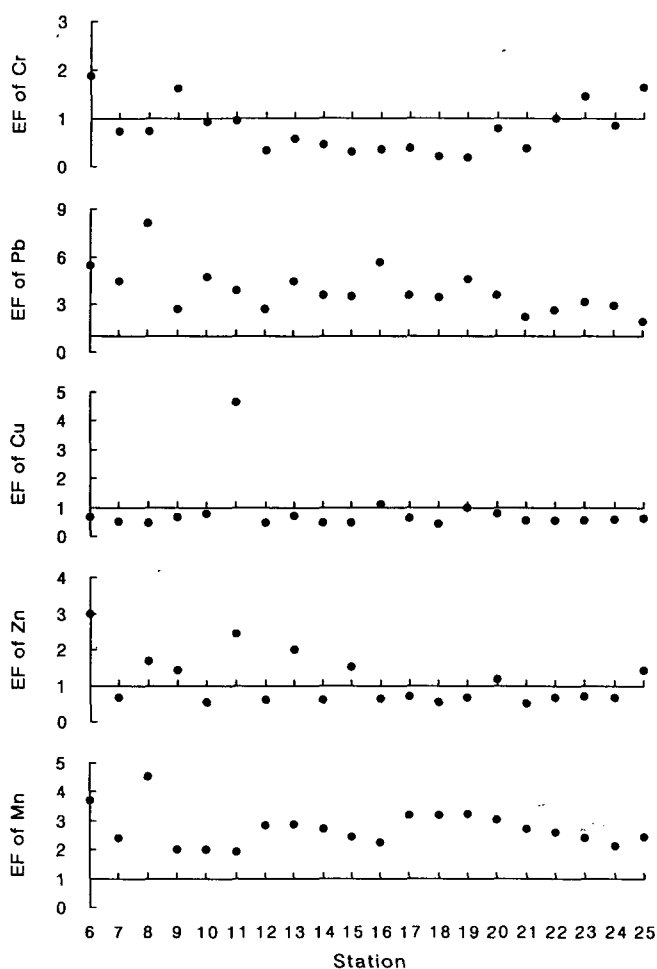


Fig. 3. The Enrichment Factor (E·F) of each analysed metal contents in sediment of Mokpo coastal area.

mg/kg dry, 12.3 mg/kg dry, 3.7 mg/kg dry and 4.7 mg/kg dry, respectively (Fig. 4). Percent of samples with the high residuals were 10%, 5% of Zn and Cu, respectively. Whereas samples higher than 1.96 SD were not detected. High level of Cu was observed at the northeast of Dali Island. High Zn was distributed in mouth of the inner Harbour and Jangja Island of the North Harbour.

The result from ratio of contents (SD/Mean), EF and residual analysis suggest that the outer harbour is contaminated by Mn, Zn, Cu and Pb. And the results from observation of trace metals distributions in the Mokpo Harbour after a strong rainfall showed that the distribution of trace metals was controlled by new sediment freshwater inputs whereas they in the inner harbor were by long-term accumulation in the outer of Mokpo Harbour.

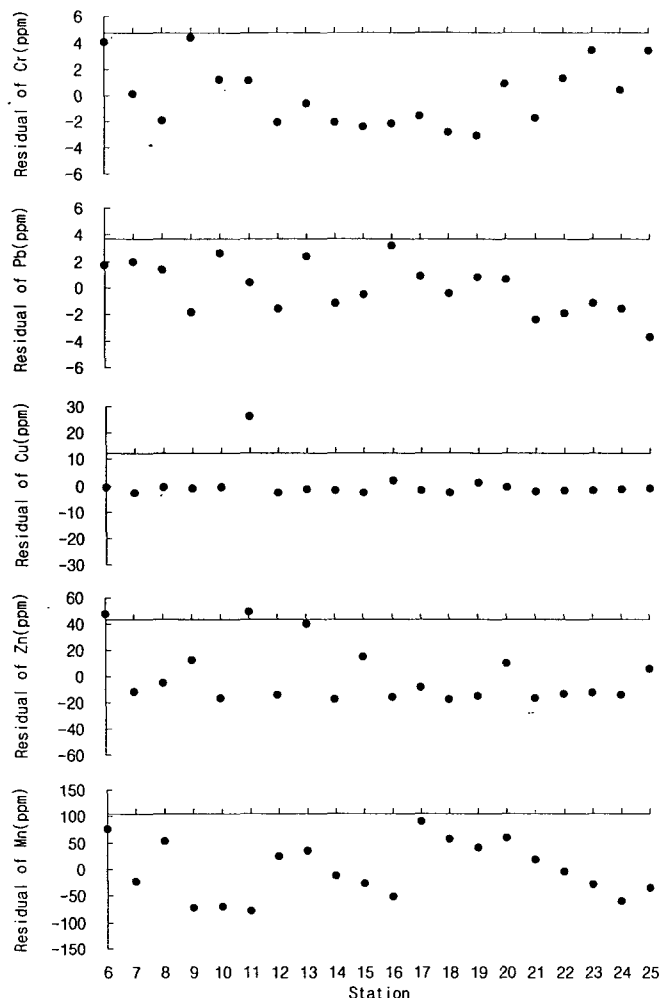


Fig. 4. Residual trace metal concentration calculated from least absolute value regression.

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