Spatial distribution and ecological risk assessment of heavy metal on surface sediment in west part of Java Sea

Hefni Effendi\textsuperscript{1,2,*}, Yusli Wardiatno\textsuperscript{b}, Mujizat Kawaroe\textsuperscript{3}, Mursalin\textsuperscript{1}, Dea Fauzia Lestari\textsuperscript{1}

\textsuperscript{1}Center for Environmental Research, Bogor Agricultural University
\textsuperscript{2}Department of Aquatic Resources Management, Faculty of Fisheries and Marine Science, Bogor Agricultural University
\textsuperscript{3}Department of Marine Science and Technology, Faculty of Fisheries and Marine Science, Bogor Agricultural University

E-mail: hefni_effendi@yahoo.com

Abstract. The surface sediments were identified from west part of Java Sea to evaluate spatial distribution and ecological risk potential of heavy metals (Hg, As, Cd, Cr, Cu, Pb, Zn and Ni). The samples were taken from surface sediment (<0.5 m) in 26 m up to 80 m water depth with Eikman grab. The average material composition on sediment samples were clay (9.86%), sand (8.57%) and mud sand (81.57%). The analysis showed that Pb (11.2%), Cd (49.7%), and Ni (59.5%) exceeded of Probably Effect Level (PEL). Base on ecological risk analysis, Cd ($E^{1;300.64}$) and Cr ($E^{1;0.02}$) were categorized to high risk and low risk criteria. The ecological risk potential sequences of this study were Cd>Hg>Pb>Ni>Cu>As>Zn>Cr. Furthermore, the result of multivariate statistical analysis shows that correlation among heavy metals (As/Ni, Cd/Ni, and Cu/Zn) and heavy metals with Risk Index (Cd/Ri and Ni/Ri) had positive correlation in significance level $p<0.05$. Total variance of analysis factor was 80.04% and developed into 3 factors (eigenvalues >1). On the cluster analysis, Cd, Ni, Pb were identified as fairly high contaminations level (cluster 1), Hg as moderate contamination level (cluster 2) and Cu, Zn, Cr with lower contamination level (cluster 3).

1. Introduction

Many human activities are conducted in the west part of Java Sea such as fishing, shipping and industrial activities. Improperly management of environmental risk of those activities could contribute to quite important effect of water contamination and pollution. The contaminants are distributed through suspended material intake carried out from the mainland by rivers flow or run off, especially the rivers are close by the coastal areas. In the marine environment, anthropogenic sources are influenced from several sources such as river discharge, deposition from the atmosphere, industrial waste input and shipping activities [1]. The contaminants movement pattern base on the surface current circulation before sinking and accumulated on the bottom sediment. The contaminant on the water column will be accumulated through the settling process into sediment, therefore sediment may be regarded as one of the pollutant storage.

Sediments act as both carriers and sinks for contaminants, reflecting the history of pollution, and could be bioindicator for aquatic ecosystems [2-4]. Investigation of heavy metal concentration on the sediment is one of method to analyze ecological risk on the sediment. Heavy metals which have low
solubility properties, will be absorbed and accumulated on the bottom sediments [5, 6]. Accumulation of heavy metals can be harmful for organism that lives on the sediment. The assessment of ecological risk is used for determining the level of heavy metals contamination on the sediment. The research aims were to identify and evaluate concentrations level, to describe spatial distribution, and to assess the ecological risk potential of heavy metals pollution in west part of Java Sea.

2. Methods

2.1. Sampling locations

Sediment samples were collected from 14 locations in west part of Java Sea. The samples were taken by Ekman grab from < 0.5 m surface layer in water depth of 26 m up to 80 meters. The maps of sampling locations are shown in figure 1.

![Figure 1. Sampling locations of sediment in the west part of Java Sea](image)

2.2. Sample analysis

Samples of sediment were analyzed at Aquatic Environment Productivity Laboratory, Faculty of Fisheries and Marine Science, Bogor Agricultural University, which has been accredited by National Accreditation Committee based on ISO 17025.

2.3. Data analysis

2.3.1 Materials composition and heavy metals concentration

Sediment materials have been identified and clarified by measuring the composition of sand and mud according to sediment grain size nomenclature of Folk triangle diagram [7]. The effect of heavy metals toxicity on sediment referred to heavy metal quality assessment based on Consensus-Based Sediment Quality Guidelines [8]. Assessment was carried out by comparing Threshold Effect Level (TEL) and Probable Effect Level (PEL) with heavy metals concentration. TEL is a threshold where the heavy metals concentration cause adverse biological effects and occur rarely, while PEL is the threshold where the heavy metals concentration cause adverse biological effects and occur frequently.

2.3.2 Spatial distribution of material composition and heavy metals

Spatial distribution of sediment composition and heavy metals concentration were visualized by software Surfer version 11. Surfer visualizes the map contour and 3 dimension base on grid (horizontal
and vertical line. This software plots tubular data xyz from each composition sediment and heavy metals concentration.

2.3.3 Ecological risk index

Ecological risk potential assessment of heavy metals referred to Hakanson method [9] with the following formula:

\[ \text{RI} = \sum_{i=1}^{n} E_i^l \times F_i^l \times C_i^l = \frac{C_i}{C_{i\text{r}}} \]  

(1)

\( E_i^l \): contamination level of heavy metal; \( C_i^l \): concentration of heavy metal on sediment; \( C_i \): reference value of heavy metal in study location; \( F_i \): ecological risk potential of heavy metal; \( C_{i\text{r}} \): toxicity response factor of heavy metal; RI (Risk Index): ecological risk potential of environment.

The factor scores on each of heavy metals according Hakanson approach [10] were: As (10), Cd (30), Cr (2), Cu (5), Pb (5), Ni (5), and Zn (1). Then, the criteria for ecological risk potential of heavy metals and environment were presented in table 1.

| \( E_i^l \) | Ecological risk criteria of heavy metal | ERI | Ecological risk criteria of environment |
|-------------|----------------------------------------|-----|----------------------------------------|
| \( E_i^l < 40 \) | Low risk | RI < 150 | Low risk |
| \( 40 < E_i^l < 80 \) | Moderate risk | 150 < ERI < 300 | Moderate risk |
| \( 80 < E_i^l < 160 \) | Considerable risk | 300 < ERI < 600 | Considerable risk |
| \( 160 < E_i^l < 320 \) | High risk | RI > 600 | Very high risk |
| \( > 320 \) | Very high risk | | |

2.3.4 Multivariate statistical analysis

Factor and cluster analysis were used for statistical multivariate analysis with software SPSS version 16.0. Correlation analysis identified correlation among heavy metals, while factor analysis simplified complex information of several variables based on similarity. Besides that, this analysis could be used for identifying the source pollution of heavy metals on the sediment, from natural source or anthropogenic contribution [10-12]. Cluster analysis is usually coupled with factor analysis to check results and to group individual parameters and variables [10]. The proximity and interrelationship among heavy metals were visualized by dendogram.

3. Results

3.1 Material Composition of Surface Sediment

The compositions of surface sediment were muddy sand (81.57%), clay (9.86%), and sand (8.57%). In general, the muddy sand distribution on the surface layer spread evenly on each station. Wave effect on surface sediment was quite low in 26-80 meters depth, then the sediment particles were accumulated in the same area.

3.2 Spatial Distribution of Heavy Metals Concentration in West Part of Java Sea

Spatial distribution pattern of heavy metals on the sediment were visualized on contour map based on concentration of each location (figure 2). There were eight heavy metals identified, those were Hg, As, Cd, Cr, Cu, Pb, Zn, and Ni. Based on the average value Ni exceeded PEL threshold, Cd and Pb exceeded TEL threshold, while Hg, As, Cr, Cu, and Zn were less then TEL threshold. On the range effect, As/Cr/Cu/Zn were distributed 100%, (figure 3 and 4), Hg was distributed 70.62% under range effect of TEL, and the others were distributed 29.4% between range effect of TEL and PEL (figure 5). The other heavy metals (Cd, Pb, Ni) were distributed 44.1%, 88.8% and 40.5% between TEL-PEL range effect, while on the range of >PEL distributed 47%, 11.2% and 59.5%.
Range effect distribution between TEL and PEL for Hg occurred in ST1, ST5 and ST8. Cd was distributed in ST2, ST3, ST4, ST5, ST7, ST11 and ST13. Pb was distributed in ST1, ST2, ST3, ST5, ST7, ST8, ST9, ST10, ST11, ST12, ST13 and ST14. Ni was distributed in ST2, ST3, ST5, ST8, ST9, ST11 and ST12. Range effect >PEL for Cd occurred in ST1, ST6 and ST14. Pb was distributed in ST6 and Ni was distributed in ST1, ST4, ST6, ST7, ST10, ST13 and ST14 (figure 4 and figure 5).

Figure 2. Spatial distribution of water depth (m), clay, sandy mud and sand percentage in west part of Java Sea

Figure 3. Heavy metals concentration average on the surface sediment in west part of Java Sea

Twenty heavy metals have been identified as essential elements for both humans and organisms at low quantities but toxic at slightly higher quantities. These include Fe, Cr, Ni, Cu, and Zn. Thereafter
Pb, Cd, Hg, As are known as toxic metals and considered the top twenty hazardous substances in the priority [1,14].

Figure 4. Spatial distribution of heavy metals As, Cr, Cu and Zn on the surface sediment in west part of Java Sea.
Figure 5. Spatial distribution of heavy metals Hg, Cd, Pb and Ni on the surface sediment in west part of Java Sea.
On the waters column Ni appears in colloidal form such as nickel nitrate, chloride and ammonium sulfate which are dissolved nickel. Concentration of Ni was more than PEL concentration (>36mg/kg) and the difference value of concentration was 1.58 kg/mg. However, this value was still less than Ni concentration in the nature (75 mg/kg) [15, 16]. The concentration of Cd was more than TEL concentration (>0.99 mg/kg), the difference value of concentration was 1.01 kg/mg. This value was greater than Cd concentration in the nature (0.20 mg/kg) [15]. Heavy metal Cd is usually mixed with other heavy metals such as Zn and Sn, for example in the mining process, Cd concentration ranged 0.2-0.4%. The natural resources of Cd are derived from volcanic activities, forest fires, and also from the activities on the sea itself. In addition, human activities also increase concentration in the atmosphere. Generally, mining activities, waste combustion, iron, steel, and phosphate fertilizer industries contribute to Cd contamination through water flow and air.

Average concentration of Pb was 60.63 mg/kg, more than TEL (>23 mg/kg). The difference value of Pb and TEL concentration was 24.63 mg/kg, that was more than available concentration on the nature (12.5 mg/kg) [15]. Around 0.1% of Pb is contained on the earth mantel. Anthropogenic activities such as mining dumping, iron and steel fusion, and agriculture waste gain the concentration of Pb through water flow. Besides that, the sources could be produced by oil mining and storage, seabed pipeline, and unused batteries disposal to the sea.

According to sediment quality assessment for aquatic organism conservation [17], high amount of heavy metals which are exceeding PEL concentration could increase possibility of biological effect to aquatic organism. Frequently effect (>50%) occurs at concentration >PEL and rarely effect (25%) occurs at concentration between TEL and PEL or <TEL.

### 3.3 Ecological Risk Index

The sequences of potential risk index of heavy metals from the highest to the lowest were Cd > Hg > Pb > Ni > Cu > As > Zn > Cr. Heavy metal Cd was categorized to high risk (HR) with the average value $E_i^2 = 284.44$, Hg was categorized to moderate risk (MR) with the average value $E_i^2 = 77.00$, the other heavy metals were categorized to low risk (LR) with the range of average value $E_i^2 = 0.02-24.25$. The toxicity of Cd has a role in the assessment of ecological risk potential. The toxicity value of Cd equals to 30 means the largest toxicity value than Pb/Ni/Cu/As/Zn/Cr, except Hg [9].

According to sampling locations, 40.58% area were categorized to very high risk (VHR), 36.24% area were categorized to considerable risk (CR) and 23.19% were categorized to moderate risk (MR). The high potential ecological risk occurred in ST14, ST6 and ST1. The sequences of potential ecological risk from the highest to the lowest were T14 > ST6 > ST1 > ST2 > ST4 > ST13 > ST3 > ST5 > ST7 > ST11 > ST10 > ST9 > ST8 > ST12 (figure 6). The contribution of Cd, Hg, and the others to ecological contribution to ecological risks of heavy metals on surface sediments were 73.88%, 18.71%, and < 6%. Based on these percentages, Cd contribution was categorized to considerable risks.

Figure 6. Spatial distribution ecological risk on RI of heavy metals on the surface sediment in west part of Java Sea
3.4 Multivariate Statistical Analysis

3.4.1 Correlation Analysis
The correlation among heavy metals (As/Ni, Cd/Ni, and Cu/Zn) and heavy metals with Risk Index (Cd/Ri and Ni/Ri) had positive correlation in the significance level $p < 0.05$ (table 2). The positive correlation shows the same source between heavy metals, dependency, and identic role during the transport [10, 18].

Table 2. Correlation matrix for heavy metals concentration on the surface sediment in west part of Java Sea

|     | Hg | As | Cd  | Cr | Cu  | Pb  | Zn  | Ni  | Ri  |
|-----|----|----|-----|----|-----|-----|-----|-----|-----|
| Hg  | 1.00 |    |     |    |     |     |     |     |     |
| As  | -0.09 | 1.00 |     |    |     |     |     |     |     |
| Cd  | -0.13 | 0.28 | 1.00 |     |     |     |     |     |     |
| Cr  | -0.45 | -0.19 | -0.51 | 1.00 |   |     |     |     |     |
| Cu  | -0.57 | -0.06 | -0.19 | 0.12 | 1.00 |     |     |     |     |
| Pb  | -0.45 | 0.06 | 0.39 | -0.45 | 0.37 | 1.00 |     |     |     |
| Zn  | -0.38 | 0.02 | -0.37 | 0.49 | **0.61** | *0.09* | 1.00 |     |     |
| Ni  | -0.27 | **0.59** | **0.71** | -0.13 | 0.08 | 0.39 | 0.17 | 1.00 |     |
| Ri  | -0.05 | 0.28 | **0.99** | -0.52 | -0.24 | 0.38 | -0.41 | **0.69** | 1.00 |

* Correlation is significant at $P<0.05$

3.4.2 Factor Analysis
Factor analysis had been applied on 9 variables for 14 sampling locations to identify the possibilities of heavy metals source on surface sediment especially for Kaiser Normalization rotation. Total variant and rotation component of heavy metals matrix explained 80.04% from total variant (figure 7). Factor 1 explained 30.20% and was dominated by Cd and Pb. Factor 2 explained 25.30% and was dominated by Cu, Pb, and Zn. Factor 3 explained 24.54% and was dominated by As, Cd, and Ni. Generally, the result of factor analysis were similar to correlation analysis result. In this case, the result of Pb was not similar between factor and correlation analysis result (coefficient correlation Pb $< 0.5$) (table 2).

![Figure 7. Screen plot of eigen values and variance total on three component factor](image)

| Component | Initial Eigenvalues | Rotation Sum of Squared/Loading |
|-----------|---------------------|--------------------------------|
|           | Total               | % of Variance | Cumulative % | Total              | % of Variance | Cumulative % |
| 1         | 3.48                | 38.61        | 38.61        | 2.72              | 30.00        | 30.00        |
| 2         | 2.36                | 26.25        | 64.86        | 2.28              | 25.30        | 55.50        |
| 3         | 1.37                | 15.17        | 80.03        | 2.21              | 24.54        | 80.04        |
3.4.3 Cluster Analysis

Average linkage in cluster analysis was used to group heavy metals and sampling locations. Based on the type of heavy metals, Cd/Ni/Pb/As were identified as high contaminant level (cluster 1), Hg was categorized to moderate contaminant level (cluster 2), and Cu/Zn/Cr were categorized to low contaminant level (cluster 3) (figure 9a). Based on locations, cluster 1 consisted of ST1, ST2, ST3, ST4, ST5, ST6, ST7, ST11, ST13, and ST14, cluster 2 consisted of ST9 and ST10, while cluster 3 consisted of ST8 and ST12 (figure 9b).

The observation areas were national and international shipping route, seabed pipeline installation, and mining area. Besides that, many industry activities are conducted especially in the coastal area of Banten Bay. Those activities may contribute to heavy metals input to the water and sediment. The availability of surface sediment (<0.5 m) which consist by mud may control heavy metal concentration on the sediment itself. Fine particles have a high ability to absorb dissolved heavy metals and deposited on the surface sediment [1].

4. Conclusions

The concentration of Ni was the highest on the surface sediment (<0.5 m) in west part of Java Sea, exceed the threshold of range effect level (>PEL). The potential risk sequences of heavy metals from the highest to the lowest were Cd>Hg>Pb>Ni>Cu>As>Zn>Cr. Cluster 1 (Cd/Ni/Pb), cluster 2 (Hg), and cluster 3 (Cu/Zn/Cr) were categorized to high, moderate, and low contaminant level. Based on locations, cluster 1 consisted of ST1, ST2, ST3, ST4, ST5, ST6, ST7, ST11, ST13, and ST14, cluster 2 consisted of ST9 and ST10, while cluster 3 consisted of ST8 and ST12.
5. References

[1] Sany SBT, Salleh A, Sulaiman AH, Sasekumar A, Tehrani G and Rezayi M 2012 Distribution characteristics and ecological risk of heavy metals in surface sediments of West Port Malaysia Environmental Protection Engineering 38 139-154

[2] Singh KP, Mohan D, Singh VK and Malik A 2005 Studies on distribution and fractionation of heavy metals in Gomti River sediments A tributary of the Ganges, India Journal of Hydrology 312 14–27

[3] Cevik F, Goksu MZL, Derici OB and Findik O 2009 An assessment of metal pollution in surface sediments of seyhan dam by using enrichment factor, geoaccumulation index and statistical analyses Environ. Monitoring Assessment. 152 309–317

[4] Devesa-Rey R, Diaz-Fierros F and Barral MT 2010 Trace metals in river bed sediments: An assessment of their partitioning and bioavailability by using multivariate exploratory analysis. Journal of Environmental Management 91 2471–2477

[5] Bai JH, Cui BS, Chen B, Zhang KJ, Deng W, Gao HF and Xiao R 2011 Spatial distribution and ecological risk assessment of heavy metals in surface sediments from a typical plateau lake wetland China. Ecological Modelling. 222 301-30

[6] Suresh G, Sutharsan P, Ramasamy V and Venkatachalapathy R 2012 Assessment of spatial distribution and potential ecological risk of the heavy metals in relation to granulometric contents of Veeranam lake sediments, India. Ecotoxicology and Environmental Safety. 84 117–24

[7] Folk RL 1980 Petrology of Sedimentary Rocks. (Austin: Hemphill Publishing) 184p

[8] CBSQG 2003 Consensus-based sediment quality guidelines Recommendations for use & application interim guidance. (Contaminated Sediment Standing Team) WT-732 40 p

[9] Hakanson L 1980 An ecological risk index for aquatic pollution control, a sedimentological approach. Water Research 14 975-1001

[10] Lu XW, Wang LJ, Li LY, Lei K, Huang L and Kang D 2010 Multivariate statistical analysis of heavy metals in street dust of Baoji, NW China Hazardous Materials 173 744-749

[11] Chen XD, Lu XW and Yang G 2012 Sources identification of heavy metals in urban topsoil from inside the Xi’an Second Ringroad, NW China using multivariate statistical methods Catena 98 73–78

[12] Yang ZP, Lu WX, Long YQ, Bao XH and Yang QC 2011 Assessment of heavy metals contamination in urban topsoil from Changchun City, China Journal of Geochemical Exploration 108 27-38

[13] Li F, Huang J, Zeng G, Yuan X, Li X, Liang J, Wang X, Tang X and Bai B 2013 Spatial risk assessment and source identification of heavy metal in surface sediment from the Dongting Lake, Middle China Journal of Geochemical Exploration 132 75-83

[14] US EPA (Environmental Protection Agency) 2004 Contamination sediment science priorities. Prepared for U.S. Environmental Protection Agency by Members of the Contaminated Sediments Science Priorities Workgroup 172p

[15] Tylor SR 1964 Abundance of chemical elements in the continental crust: a new table Geochimica et Cosmochimica Acta. 28 1273-1285

[16] Moore JW 1991 Inorganic contaminant of surface water: research and monitoring priorities (New York: Springer-Verlag) 334p

[17] Canadian Council of Minister of the Environment (CCME) 2001 Canadian sediment quality guidelines for the protection of aquatic life: Introduction. (Canada: Winnipeg)

[18] Saeedi M, Li LY and Salmanzadeh M 2012 Heavy metals and polycyclic aromatic hydrocarbons: pollution and ecological risk assessment in street dust of Tehran Journal of Hazardous Materials 227–228 9–17