DISTRIBUTION OF METALS IN CISANGGARUNG ESTUARY SEDIMENT, WEST JAVA, INDONESIA

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ABSTRACT

Volcanic activities have influenced the Cisanggarung estuary in western Cirebon Regency, altering metal concentrations in the bottom sediment. Observation of metal content in the ocean there was carried out in August 2009. Sediment samples were collected at 16 stations along the Cisanggarung coastline. The aim of this work was to determine the spatial distribution of Cd, Cu, Pb and Zn in the sediment of the Cisanggarung estuary. Sediment was destructed using 3 acids: nitric acid, chloride acid and peroxide acid, which was then analyzed by Flame Atomic Absorption Spectrophotometry based on the US EPA 3050b method. The highest concentrations of Cd, Cu, Pb and Zn in the sediment were 0.73 mg/kg dry weight, 31.4 mg/kg dry weight, 23.9 mg/kg dry weight and 143 mg/kg dry weight, respectively. The metals in the sediment had accumulated near the shoreline, up to five kilometers away from the river mouth, indicating that terrestrial area and sediment fractions influenced their distribution.

Keywords: Cisanggarung estuary, sediment, metals, distribution.

INTRODUCTION

Heavy metal contamination of sediment can significantly degrade aquatic ecosystems (Honglei *et al*., 2008; Lepland *et al*., 2010). Natural and anthopogenic activities release contaminants such as metals into the environment and this is a threat to aquatic ecosystems (Wang *et al*., 2011). From both environmental and ecological viewpoints, studying the transfer of these contaminants to the marine habitat is imperative and so the distribution of contaminants has been studied extensively in various regions in the world (Roussiez *et al*., 2011). Their release from bottom sediment can make them enter into the aquatic ecosystem (Cabon *et al*., 2010) and may bring serious problem to the ecosystem. Inspite of differences in their toxic effects, metals are hazardous material in high concentrations and their content in bottom sediment can be recognized as an indicator of ecosystem health (Sakellari, 2011; Ren-Ying *et al*., 2007).

Sediments are important in the assessment of metal contamination in natural waters (Soares *et al*., 1999). Bottom sediment granulation is one of the reasons for thevariation in pollution levels (Chatterjee *et al*., 2007; Skorbilowicz and Skorbilowicz, 2011). Metals are adsorbed in differently, depending upon the binding capabilities of the different sediment textures (Ip *et al*., 2007). Metals tend to concentrate in particles of silt-clay size and this fraction is dispersed in waters by suspension (Villaescusa-Celaya *et al*., 2000).

The Cisanggarung estuary is located in the Cirebon Regency, Indonesia and this area has been influenced by volcanoes near the source of the river. Metals released by volcanic activities affect this estuary and enriched metals potentially disturb organisms there (Sanusi, 2005). In addition, anthropogenic activities, including farming, are increasing near this estuary (Badan Pusat Statistik Kabupaten Cirebon, 2013). However, metal concentrations in Cisanggarung estuary have not yet been examined although anthropogenic activities

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have become a major source of metal input into the aquatic environment in various areas in the world (Ashton *et al*., 2010; Freret-Meurer, 2010). The main purposes of this work was to determine Cd, Cu, Pb and Zn distribution in the marine sediment near the Cisanggarung estuary.

MATERIAL AND METHOD

Study site

The metal concentration in the Cisanggarung estuary sediment was measured at 15 sampling points in August 2009 (Fig. 1). The Cisanggarung river originates on the volcano Mount Cereme, and the river mouth and shoreline near the Cisanggarung estuary were chosen as a sampling site because the source of the metal entering the river sediment was known. Surface sediment samples were collected using a ponar grab then stored in a high density polyethylene (HDPE) box and kept cool while in the field (Yu *et al*., 2010).

Laboratory analyses

Analysis of Cd, Cu, Pb and Zn concentrations in the sediment was carried out using the US EPA 3050b method. HNO_3 (1+1) was added to a gram of dry sediment then concentrated HNO_3 was poured into a mixture of solution. After heating the solution, 10 ml in maximum volume of 30% of H_2O_2 was added by dropper. In the last step of digestion, 10 ml HCl was poured in and the solution was heated for 15 minutes. Cooled sample solution was filtered using Whatman filter paper. All the glassware was rinsed in HNO_3 (1+1) for 24 hours before it was use to ensure the analysis was ultrapure.

The reference material was analyzed to assure the accuracy of the data. The digestion of the reference material was conducted using a similar procedure to the sample digestion. HNO_3, H_2O_2 and HCl were added to the reference material and the solution produced was filtered using celulose-nitrate Whatman filter paper. Sample and reference materials were analyzed with a Flame Atomic Absorption Spectrophotometer Merck Varian type SpectrAA 20.

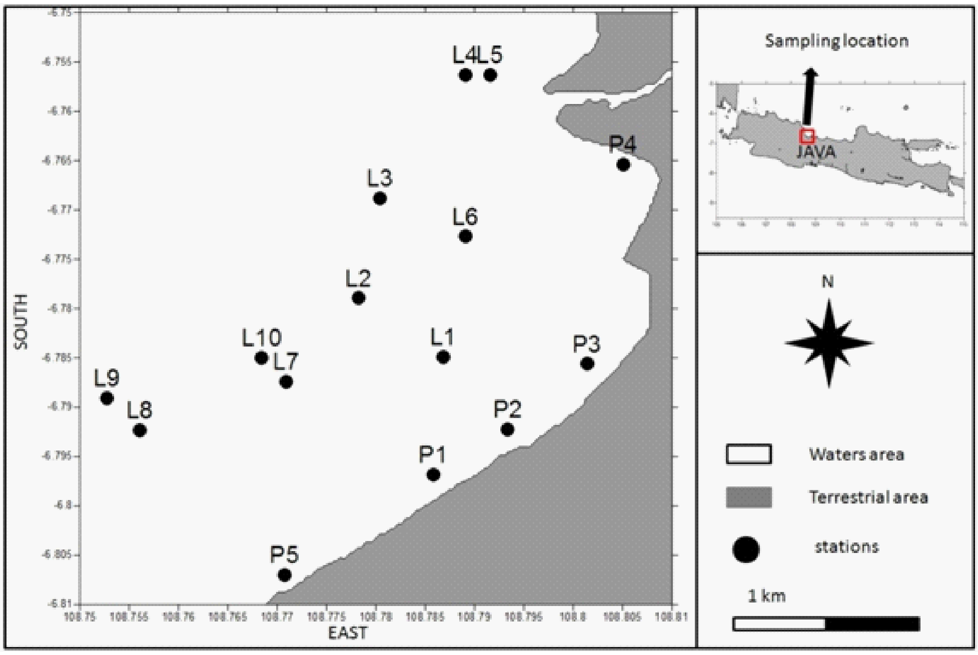

Figure 1. Sampling point in Cisanggarung Estuary, West Java

Data Analyses

STATISTICA version 6.0 software was utilized for data analysis. Clustering analysis was employed to describe the data set of the four metals analyzed. Ward's method was used to calculate Euclidean distances and a dendogram was drawn for the sampling stations. To understand the influence of the sediment fraction on metal distribution, Principal Component Analysis was used.

RESULTS

Cd in the sediment was distributed evenly in the estuary, with concentrations ranging between 0.53-0.73 mg/kg dry weight. The highest concentration of Cd was detected off the coast (station P3) at 0.73 mg/kg. Stations P5 and station L5 had the minimum Cd concentrations, 0.53 and 0.54 mg/kg dry weight, respectively (Fig. 2A). Cu concentration in sediment was from 17.28 (station L8) to 31.37 mg/kg dry weight (station L3) and Pb concentration in the sediment was 7.01 (station L4) to 23.94 mg/kg dry weight (station L3) (Fig. 2B; Fig. 2C). Zn concentration in sediment ranged from 65.23 (station L4) to 142.51 mg/kg dry weight (station P1) (Fig. 2D).

On the basis of metals concentration in sediments, 3 clusters were depicted in the Cisanggarung estuary: Cluster I (stations L1, L2, L7, L5,

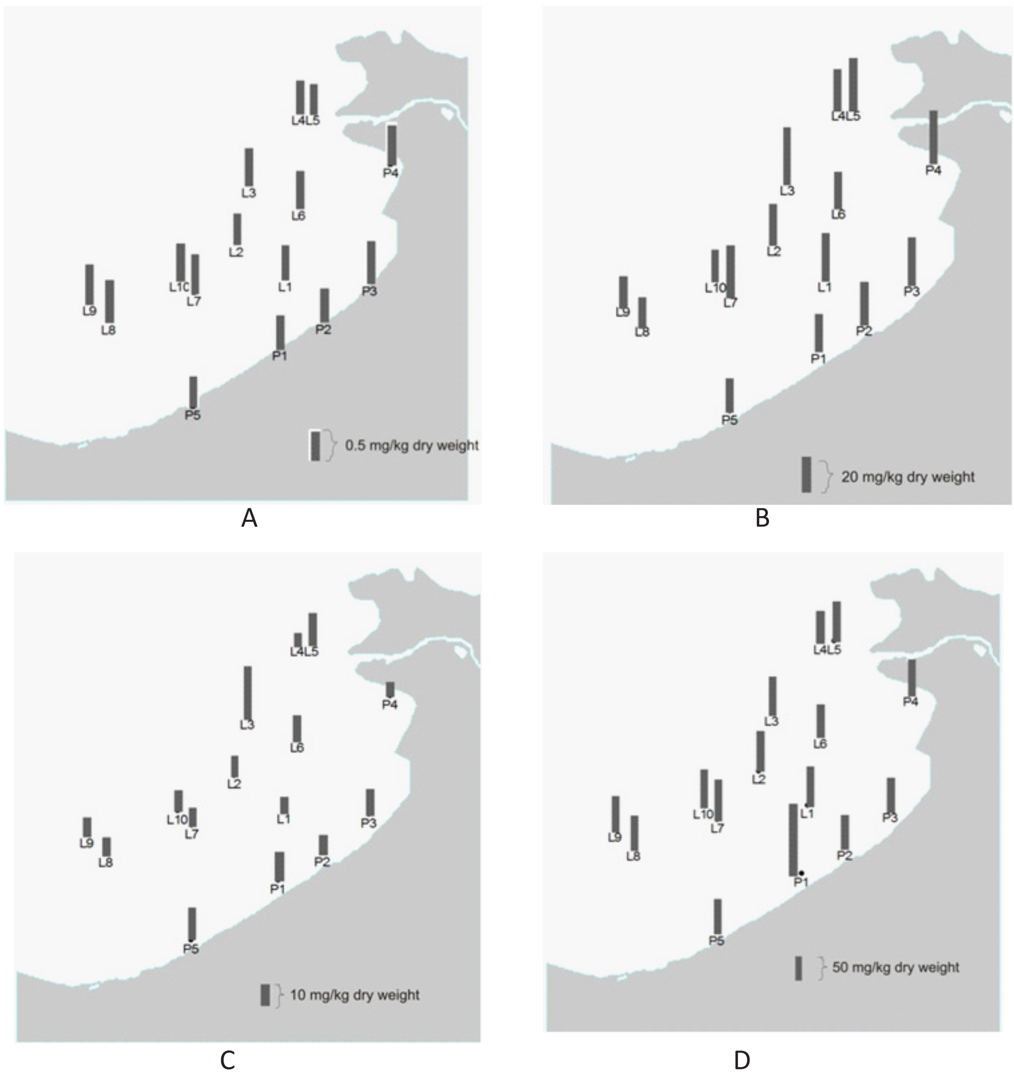

Figure 2. Distribution of Metals in sediment in Cisanggarung Estuary, Cirebon, West Java. (A) Cd distribution, (B) Cu distribution, (C) Pb distribution, (D) Zn distribution.

L3), cluster II (stations P2, P3, L4, L6, P5, P4, L8, L9, L10) and cluster III (station P1) (Fig. 3).

The Cisanggarung river that flows into this estuary is reponsible for the distribution of the sediment fraction. Stations L4 and L5, proximal to the river mouth, were observed to have a coarse to very coarse sediment composition. (Fig. 4).

Principal Component Analysis revealed that Cd, Cu and Zn tend to bind in small particles, the fine fraction of sediment, like clay and silt. Cd and Cu adsorbed in very fine sand while Zn accumulated in clay. A different trend was indicated by Pb, very coarse sand contained Pb more than the other fractions (Fig. 5).

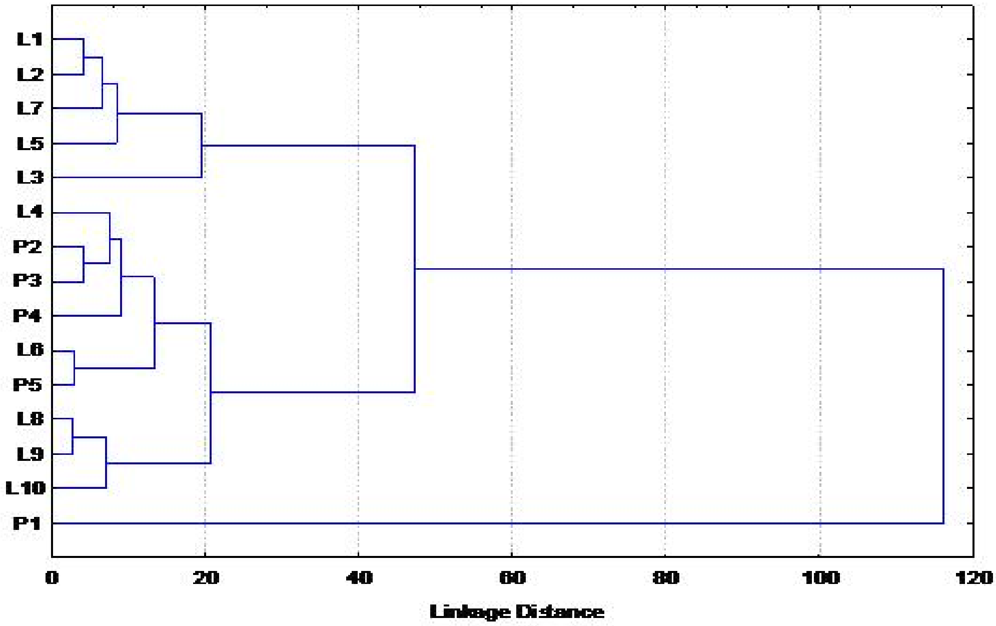

Figure 3. Dendogram of sampling stations in Cisanggarung Estuary.

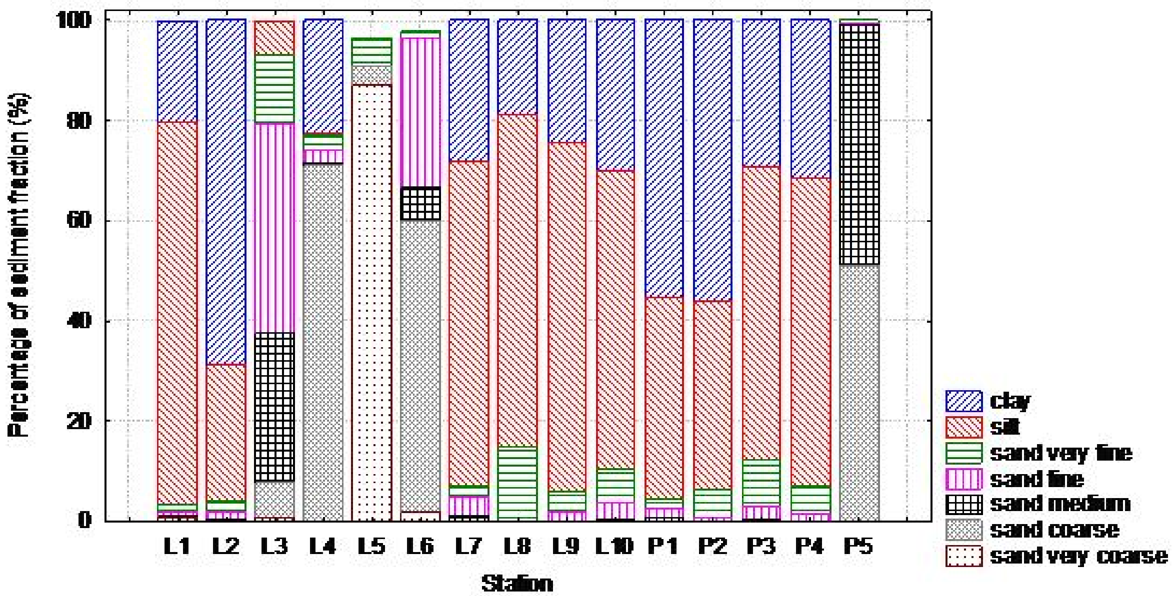

Figure 4. Percentage of sediment fraction in each station.

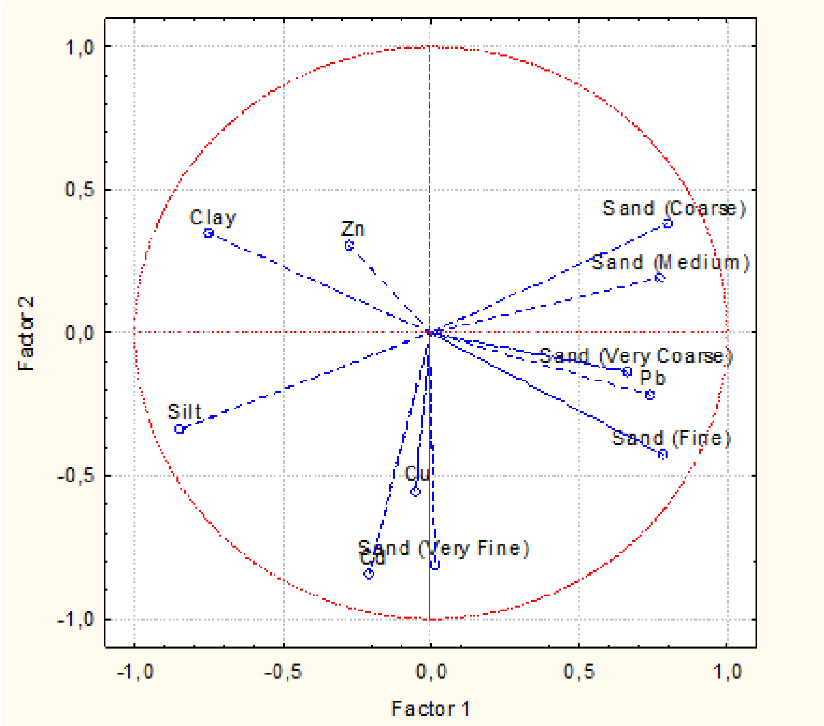

Figure 5. PCA for metals in sediment and sediment fraction.

DISCUSSION

Cluster I (station L5, L1, L2, L7, L3) is the group with a low concentration of metals. Despite its location near shoreline, very coarse sand to coarse sand dominated the sediment fraction in station L5. The Cisanggarung river runoff includes a large amount of volcanic materials, thus tidal surge could play an important role in the distribution of metals in the sediments (Alagarsamy, 2006; Shi *et al*., 2006; Dessai *et al*., 2009). The texture of surface-layer sediments changes constantly due to current and turbulance, bioturbation of benthic organisms, or human activities like trawling (Everaarts and Fischer, 1992; Zhang *et al*., 2001; Shi, 2010; Webster and Ford, 2010). Stations located far away from the shoreline (station L1, L2, L7, L3) indicated low concentrations of metals in the sediment inspite of having a fine sediment fraction. Diffusion and resuspension probably reduced the metal concentrations in the sediment. Eggleton and Thomas (2004) explained that natural events such as tidal movement and storms can remobilize the sediment-associated contaminants.

High concentrations of Cd, Cu, Pb and Zn were detected in cluster II, near-shoreline stations (station P2, P3, P4, P5) and in some far-shoreline stations (station L4, L6, L8, L9, L10). Near-shoreline stations tend to have a fine sediment fraction. Furthermore, these stations might have been influenced by terrestrial sources of contamination. In other research, sediment contaminated by metals from land and anthropogenic waste enriched estuarine sediment by a process of soil leaching and waste disposal (Dassenakis *et al*., 1995; Emmerson *et al*., 1997; Spencer, 2002; Vicente-Martorell *et al*., 2009; Xia *et al*., 2011). Hence, anthropogenic activities become a major source of metal input into the estuary. Research in the Pearl river estuary (China) reported the enrichment of heavy metals in sediments was largely controlled by anthropogenic pollution (Ye *et al*., 2012). Station P5 was grouped in a different cluster, cluster I, due to the extremely high Zn concentration (up to 143 mg/kg dry weight) detected. Anthropogenic activities on land may contribute to the high accumulation of Zn. Zn is mainly used in the production of noncorrosive alloys, brass, galvanizing steel, fungicide, white pigments in rubber processing, to coat photocopy paper, iron products and sometime Zn is used therapeutically in human medicine (Eisler, 1993).

Cd, Cu and Zn tend to bind into very fine sand-clay sediment. The size of particles becomes an important factor in controlling the metals-binding capability of sediment (Pandarinath and Narayana, 1992; Van Alsenoy, 1993; Jones and Turki, 1997). Finer particles provide a greater specific surface area than coarse ones and that allows more space on the surface for metals to bind to and hence enables more metal content in the sediment. Furthermore, dense sediment bed, defined by its fine particles, might cause a slower diffusion of metals. Without an external trigger, sediment resuspension, or tidal effect, released metals remain in the sediment bed and probably readsorb onto the particle surface. This limited mobility causes more metal content in finer sediment. A greater particle size, indicated by the porous texture of bed sediment, provides a greater chance of metals diffusing into the upper water column. Metals in Limski Kanal (North Adriatic Sea) were reported to concentrate in the finest clay/silt fraction whereas metal concentrations in the coarser fraction varied depending on their chemical characteristics (Martinćtić *et al*., 1990).

Pb showed a different trend compared with other metals, as it tended to bind with the coarser sediment fractions. Station L3, located far away from the shoreline, had the highest concentration of Pb at 23.9 mg/kg dry weight. The physico-chemical properties of water and sediments could provide a plausible explanation for this phenomenon. Metals tend to precipitate in saline-based water (Cotton and Wilkinson, 1979) and the deposition of dissolved and particulate Pb may contribute to enrichment of Pb in sediment. A similar phenomenon was reported in the Severn estuary and the Bristol Channel, U.K., where, at some sites, Cd was observed to asssociate with the coarser sediment fraction (Duquesne *et al*., 2006).

The range of the concentrations of Cd, Cu, Pb and Zn in the riverine-estuarine sediments of the Cisanggarung estuary was found to be similar to other studies in the literature. In the same kind of tropical estuarine system, Marmolejo-Rodríguez *et al* (2007) reported that metal concentrations in sediment in Marabasco estuary (Mexico) varied between 0.05-0.34 mg/kg (Cd), 0.7-31 mg/kg (Cu), 2-18 mg/kg (Pb) and 53-179 mg/kg (Zn). In Baja California (Mexico) and California (USA), the concentration ranges (in mg/kg) of the metals in sediments were: 0.08-0.64 mg/kg (Cd), 4.9-23 mg/kg (Cu), 6-21 mg/kg (Pb) and 39-188 mg/kg (Zn) (Villaescusa-Celaya *et al*., 2000).

Cisanggarung estuary sediment indicated a relatively lower concentration of metals than in the Hudson River estuary, the highly populated urban center around New York Harbor. The concentration ranged from 0.18 to 2.29 mg/kg dry weight (Cd), 18 to 149 mg/kg dry weight (Cu), 24 to 177 mg/kg dry weight (Pb) and 101-257 mg/kg dry weight (Zn) (Feng *et al*., 1998).

The concentrations of metals in the Cisanggarung estuary sediments were still below the values indicated in sediment quality guidelines. For example, comparison with the PEL values according to the Canadian Council of the Ministers of the Environment (1999) (4.2 mg/kg for Cd; 108 mg/kg for Cu; 112 mg/kg for Pb, and 271 mg/kg for Zn) suggests that the metals levels revealed in this study do not affects marine organisms.

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