Fate and spatial distribution of Pb, Cd, Cu and Zn in the water column and in the surface sediment of Indonesian Estuary (Citarum River Estuary)

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Abstract. The Citarum River Estuary is an area where mixing among seawater and freshwater occurs since directly connected with the Java Sea. The different condition in estuary will affect heavy metal concentrations in the dissolved phase and suspended/deposited in sediment phase. In this study, fates and distributions from Pb, Cd, Cu and Zn were analyzed along 2 km from estuary mouth. Samples were analyzed by Flame AAS. The study began with water/sediment quality assessments, and fate and distribution analyses with Adsorption Capacity Indices (ACI), Dissolved Transport Indice (DTI), K_{oc}, K_{ow}, spatial distribution in water (3D) and sediment (2D) using MATLAB, and statistical analysis (ANOVA/Kruskal-Wallis). In conclusion, heavy metals sequence from the highest pollution level in water were: Zn > Pb > Cu > Cd, and in sediment were: Cd > Pb > Zn > Cu. Pb, Cd, Cu, and Zn had a tendency to be in sediment compared to water (ACI = 99.69% – 99.89%; DTI = 0.109% – 0.309%), slightly mobile (log K_{oc} = 3.11 – 3.58), and hydrophobic (log K_{ow} = 3.35 – 3.87). Pb and Cd showed significantly different concentrations in water columns (surface/midst/base) (p<0.05), in contrast to Cu and Zn. Pb, Cd, Cu, and Zn had insignificant concentration difference based on zone division from estuary mouth, both in water and sediment.

1 Introduction

The Citarum River is a polluted river in the world subsequent to the River Sarno, Italy [1]. According to Southeast Asia Greenpeace and *Wahana Lingkungan Hidup Indonesia* (Walhi) on Indonesian Minister of Health (2018), heavy metals are one of the main contaminants that affect to the water quality of the Citarum River.

The downstream area of the Citarum River is an area that has a considerable opportunity to cause to be experienced the negative impacts of the heavy metal presences. Those conditions can occur because the pollutant in the upstream will stream following streamline area to the downstream area of the river. The downstream area (also called "estuary") of Citarum River is located in Bekasi Regency and is directly related to the Java Sea so that there will be a mixing of the seawater and the freshwater. The mixing processes will influence on the fate and the distribution of heavy metals through the processes of adsorption-desorption, deposition-resuspension, and distribution which are influenced by physicochemical parameters in the estuary. Estuary is characterized by the high levels of turbidity, salinity, and ionic strength [2]. Increased ionic strength causes stronger tensile between particles so that the ability to adsorb heavy metals gets stronger. Najamuddin (2017) argues that Pb is absorbed in salinity 12-30 ‰ and Zn in 0.5-3.0 ‰ in Jeneberang River Estuary, Makassar [3].

Based on the background, the researcher conducts the study with the deeper study of the fate and distribution of heavy metals found in the Citarum River Estuary. The purposes of this study were to analyze the fate of heavy metals and the water-sediment distribution, as well as to analyze the concentration distribution of heavy metals due to the mixing in the estuary.

2 Methodology

The study was conducted in the Citarum River Estuary, Muara Gembong District, Bekasi Regency, West Java Province. Geographically, the location was located between 5° 56' 25.80" S to 5° 56' 8.13" S and 106° 59' 18.19 " E to 107° 0' 19.57" E. The study was conducted on April 28, 2018 (at 13:46 – 16:15) and on April 29, 2018 (at 11:07 – 13:04) during the rainy season and the low tide condition.

The sampling points consisted of 3 zones (1st zone: the zone closest to the Java Sea which had high salinity; 2nd zone: the zone between 1st zone and 3rd zone; as well as 3rd zone: the zone with the farthest distance from the

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Java sea with low salinity) (**Fig.1.**) Water sampling was carried out at the 3 depth layers, such as the surface, the middle, and the base layer **(Fig.2.),** and the sediment sampling only on the surface layer.

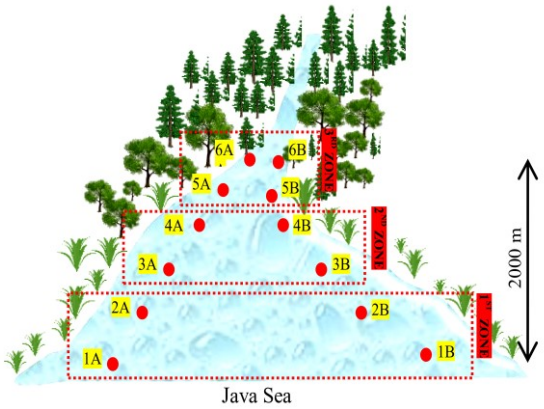

Fig.1. Sampling points and zone division

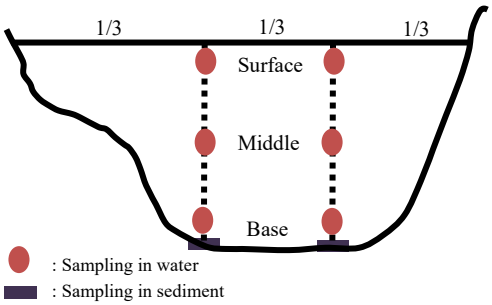

Fig.2. Cross section of sampling points

2.1 Water Sampling

The water samplings were carried out using a horizontal water sampler. According to Standard Method for the Examination for Water and Wastewater 22nd Edition (2012), water samples were preserved by adding nitric acid (HNO_3) with pH <2 by 6-7 drops and by cooling at 4ºC.

2.2 Sediment Sampling

The sediment samplings on the surface layer were carried out using an Eckman Grab Sampler. According to the Ohio Environmental Protection Agency (2015): the Sediment Sampling Guide and Methodologies in the Sample Preservation Section, the sediment samples for all analyzes such as heavy metals were preserved by cooling at 4ºC.

2.3 Data Analyzes

The analyzes of water pollution levels were carried out based on the Pollution Index (PI) method. The Pollution Index (PI) was used to determine the level of pollution relative to the permissible water quality parameters with the following equation.

$$PI_j = \sqrt{\frac{(\frac{Ci}{Lij})_M^2 + (\frac{Ci}{Lij})_R^2}{2}} \quad (1)$$

Where PI was the Pollution Index for designation j, Ci was the concentration of water quality parameter i, Li was the concentration of water quality parameter i listed in the designation quality standard j, while M was the maximum, and R was the average. PI index class consisted of 4, with a score of $0 \leq PI \leq 1.0$ had good water quality; $1.0 \leq IP \leq 5.0$ was slightly polluted; $5.0 \leq PI \leq 1.0$ was moderately polluted, and $PI \geq 10.0$ was heavily polluted.

The pollution levels in the sediment were done by calculating contamination factor (CF) with the equation in Doulah et al (2017), as in the equation below [4].

$$CF = \frac{C\ compound}{C\ background\ value} \quad (2)$$

Where, CF was the contamination factor, $C_{compund}$ was the concentration of heavy metals in the sediments, and the $C_{background\ value}$ was the background concentration of heavy metals. CF value of <1 indicated a low level of contamination, $1 \leq CF < 3$ indicated a moderate level of contamination, $3 \leq CF < 6$ indicated a high level of contamination, and CF ≥6 indicated a very high level of contamination.

The fate and distribution analyzes of heavy metals were carried out by ACI and DTI analysis with equation in Najamuddin (2016) [5], analysis of the coefficient of organic-carbon (K_{oc}) and octanol-water (K_{ow}), and anaysis the real differences in the heavy metals (Pb, Cd, Cu, and Zn) in the 3 depth layers and the 3 zone divisions accompanied by advanced analysis of Post Hoc for ANOVA was Tukey HSD and for Kruskal-Wallis was Dunn's test using IBM SPSS Statistics 24 software.

The adsorption capacity of compounds was expressed by Adsorption Capacity Indice (ACI), and the dissolved transport index was expressed by Dissolved Transport Indice (DTI). ACI and DTI were calculated by the equation stated by Sanusi (2006) in Najamuddin (2016), as follows [5].

$$ACI = [Cs/(Cs+Cw)] \times 100\% \quad (3)$$

$$DTI = [Cw/(Cs+Cw)] \times 100\% \quad (4)$$

The heavy metals had the tendency to experience partitioning with the organic fractions in the sediments, and the adsorption of heavy metals in the sediments tended to occur due to the presences of organic carbon (C-organic) material. The level of compound mobilities in the water was supported by K_{oc} values. The following was the equation of the organic-carbon coefficient (K_{oc}).

$$K_{oc} = K_D/f_{oc} \quad (5)$$

The hydrophobicity or the hydrophilic nature of a compound was expressed as K_{ow}. The octanol-water coefficient value was calculated using the regression model to estimate the log K_{ow} from the Log K_{oc} value,

the equation was obtained from Baker et al. (1997) in Boethling and Mackay (2000) which stated that the equation applied to various chemical compounds. The model equation was as follows [6].

$$\text{Log } K_{oc} = 0{,}903 \text{ log } K_{ow} + 0{,}094 \qquad (6)$$

ANOVA/Kruskal-Wallis analysis to analyze the real differences in the heavy metals (Pb, Cd, Cu, and Zn) in 3 depth layers and 3 zone division accompanied by the advanced analysis of Post Hoc for ANOVA was Tukey HSD and for Kruskal-Wallis was Dunn's test using IBM SPSS Statistics 24 software.

The spatial distributions were made by MATLAB software, with the function "pcolor3 (X, Y, Z, V)" for the water compartment, which was the function for plotting the volume of 3D data. For the sediments, the function used was "pcolor (X, Y, V)", that was function for plotting 2D square patches defined by 3 variables.

3 Results and Discussion

3.1 Water and Sediment Quality

According to the Governor Decree of West Java No. 39 of 2000, the Citarum River was used as the raw water for drinking water (Class B), fisheries and animal husbandry (Class C), agriculture and others (Class D). **Tab1e 1** shows the results of Pollution Index values and heavy metal pollution categories.

Table 1. PI values indicating the water quality of Citarum River Estuary based on Pb, Cd, Cu, and Zn concentrations

Heavy Metals	PI value	Pollution Category/ Water Quality
Pb	4.358	Slightly Polluted
Cd	0.310	Good Water Quality
Cu	2.382	Slightly Polluted
Zn	6.230	Moderately Polluted

The table above shows that the Cd has a good water quality with PI values in the range of 0-1. Pb and Cu are in the slightly polluted with PI values in the range of 1-5, and Zn is in the moderately polluted with PI values in the range of 5-10.

The sediment quality assessments are done by calculating the contamination factor, where these assessments use the background value shale for each type of heavy metal from Turekian and Wedepohl (1961) [7]. The results of the sediment quality assessments for each heavy metal can be seen in **Table 2** below.

The **Table 3** below shows that Cd in the sediments is categorized as very high contaminated. The heavy metals in the sediments included in the moderate level contamination based on the CF value are Pb and Zn, and those included in the low level contaminantion based on the CF value are Cu.

Table 3. Sediment quality in Citarum River Estuary

Heavy Metals	Contamination Factor (CF)		Background value
	CF Value	Level Contamination	Turekian and Wedepohl (1961)
Pb	2.20	Moderate level	20
Cd	8.81	Very high level	0.3
Cu	0.56	Low level	45
Zn	1.46	Moderate level	95

The sequence of heavy metals in the sediment from the highest polluted are Cd > Pb > Zn > Cu. The order of contamination in sediments is different from that in the water column, where the order of types of heavy metals from the most polluted are Zn > Pb > Cu> Cd. The contamination of heavy metals in sediments originates from heavy metals in the water column undergoing the process of deposition. Based on an analysis of heavy metal contamination level in the water and in the sediments, heavy metal contamination in the sediments tends to be higher than in the water.

3.2 Fate in Citarum River Estuary

ACI and DTI values are used to determine the solubility level of heavy metal. If the ACI value of heavy metals is greater than the DTI, the solubility of the metal is high. Heavy metals that has high solubility will be easily adsorbed by particulates and deposited to the bottom of the water. The average value of the ACI and DTI percentage can be seen in the table below.

Table 4. The average of ACI and DTI percentage

	Pb	Cd	Cu	Zn
ACI (%)	99.69	99.89	99.87	99.85
DTI (%)	0.309	0.109	0.131	0.155

Based on the table above, the average value of ACI percentage of all types of heavy metals ranges from 99.69% - 99.89%, and the average value of DTI percentage ranges from 0.109% - 0.309%. Those results show that heavy metals in the water of the Citarum River Estuary tend to be in the form of particulates that were deposited to the bottom layer and accumulate into the sediments, whereas only a small portion of heavy metals contained in the water column as the dissolved form. A similar result is stated by Najamuddin (2017) that Pb and Zn, has an ACI average value of 99.94% and 99.99%, as well as DTI of 0.06% and 0.01% [3].

The level of heavy metal mobilities are based on the organic-carbon coefficient (K_{oc}). According to

Armanpour and Bing (2015), the K_{oc} value for very mobile was <15 l / kg; for mobile which is 15-75 l/kg, for moderately mobile which is 75-500 l/kg; for slightly mobile which isi 500-4000 l/kg; and immobile which is >4000 l/kg [8]. **Table 5** shows the organic-carbon coefficient (K_{oc}) of Pb, Cd, Cu, and Zn.

Table 5. Organic-carbon coefficient (K_{oc})

	Log K_{oc} dan K_{oc}			
	Pb	Cd	Cu	Zn
Log K_{oc}	3.11	3.58	3.55	3.44
K_{oc}	1294	3775	3557	2760

Table 5 above shows that the average K_{oc} value for all types of heavy metals (Cd, Cu, Zn, Pb in sequence from the highest K_{oc}) has the level of mobility that is slightly mobile. Pb, Cd, Cu, and Zn found in the Citarum River Estuary has slight mobility so that Pb, Cd, Cu, and Zn in the Citarum River Estuary are easily adsorbed, degraded and settle in the sediments. Therefore, heavy metals tend to be in the sediments rather than in the water, and are likely to have high bioavailability in the organisms. Heavy metals in the sediments can accumulate to living organisms when foraging in the sediments.

The octanol-water coefficient (K_{ow}) also indicates the hydrophobic nature of the chemical compound. According to Karickhoff et al. (1979) and Noordsij et al. (2003), hydrophobic compounds (low solubility in the water) have a log K_{ow} value >0 and hydrophilic compounds (high solubility in the water) have a log K_{ow} value <0 [9].

Table 6. Octanol-water coefficient (K_{ow})

	Log K_{ow} dan K_{ow}			
	Pb	Cd	Cu	Zn
Log K_{ow}	3.35	3.87	3.84	3.72
K_{ow}	2250	7365	6894	5206

Table 6 above shows that Pb, Cd, Cu, and Zn have a log K_{ow} value >0 (positive), meaning that Pb, Cd, Cu, and Zn have the hydrophobic or lipophilic character (prefer fat) so that they have the solubility higher in the octanol area than in the water. Heavy metals that have a high log K_{ow} value will have the potential to process the bioconcentration of heavy metals in the aquatic organisms. According to Sikdar and Kundu (2018), bioconcentration in lipid tissue occurs in the process of exchanging compounds from the water column (uptake of chemical compounds not through food or oral consumption) and the degree of bioconcentration is influenced by the hydrophobicity of the chemical compounds obtained from the evaluation of the octanol-water coefficient value [10].

3.3 Spatial Distributions

In **Fig.3**, it is clear that most high concentrations of heavy metals are found in the base layer. Those indicated that the addition processes originated from the surface sediment. However, the vertical distribution pattern is only clearly visible at the mouth of the estuary (0 m) because the location was most affected by the stirring process from the sea tidal effect so that the resuspension sediment and desorption processes are greater (see the distribution of Cd). the results of ANOVA/Kruskal-Wallis analysis show that only Pb and Cd have significant differences in the average concentration in 3 layers of the water which were significant (p<0.05) and significant differences found in the middle-surface and base-surface layers based on the Post Hoc test. Those results indicated that Pb and Cd have increased concentrations with increasing the depth from the surface to the bottom of the water. The high concentrations in the bottom of water come from the surface sediment that were experiencing resuspension (Distribution of Pb and Cd can be seen in **Fig.4**). Sediment resuspension will increase TSS concentration and turbidity. Heavy metals that were bound with TSS are desorption, resulting the increasing of heavy metals dissolved in the water colums.

Zhang et al. (2018) argue that in the estuary environment, heavy metals can be partitioned into particle phases of the sediment, where heavy metals can be absorbed by particulate matter in the particulate phase and deposited into the sediments, while metals can be released back into the water column from the sediment by resuspension [11]. Dippong et al. (2017) suggest that the concentration of Pb and Cd had increased with increasing the depth from the surface to the bottom of the water which was thought to be due to the release of metal ions into the water column based on the oxidation-reduction reaction in the sediment [12].

In contrast to heavy metals Cu and Zn, which do not have a significant differences in depth layers because the Cu and Zn concentration in the water column were thought to not only originate from the process of remobilization of sediments, but it was suspected that there were still anthropogenic sources from community activities that cause the concentration of Cu and Zn metals to fluctuate in the water column. This was also supported by the pollutant index of Cu which was classified as slightly contaminated in the water column, and Zn which was classified as moderately polluted in the water column.

Cu pollutants that were high are dominant in the surface layer and middle layer of Citarum River Estuary. It was also suspected that high rainfall in April 2018 caused the concentration of heavy metals entering the water body to increase due to the erosion of land and heavy metal sources presented in the atmosphere that entered the body of water through rain.

While zinc (Zn) was thought to originate from effluent domestic waste because Zn was contained in shampoos and detergent formulas. In addition, Zn can also be sourced from dyes in ship paint, so that Zn in estuary water whose livelihood as fishermen was thought to be caused by the release of anti-fouling coatings on ship paints around the study area.

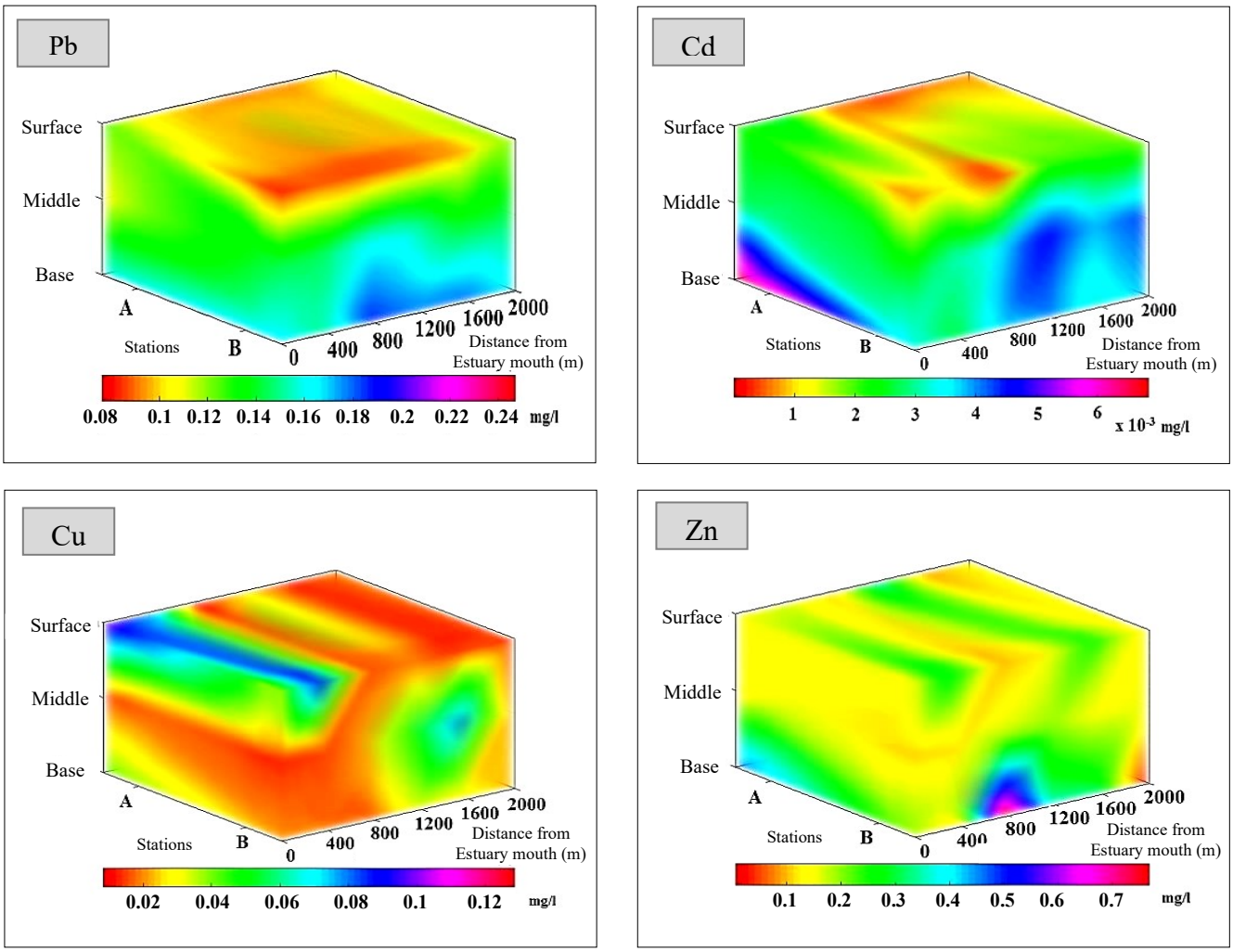

Fig. 3. Spatial distributions of Pb, Cd, Cu, and Zn in water column (3-Dimensional)

Fig. 4. shows that on the surface sediment, the distribution of Pb shows a varied pattern. The highest Pb concentration (51.995 mg/kg) was at the 6A sampling point that was 2000 m away from the mouth of the estuary and the lowest (36.510 mg/kg) was at the sampling point 800 m - 1200 m from the mouth of the estuary (sampling point 4A - 5A).

On the surface semdiment, the distribution of Cd concentrations varies. At a distance of 400 m from the mouth of the estuary, the lowest Cd concentration was found at station B, while at a distance of 800 m from the mouth of the estuary, the highest Cd concentration was found at station B. At a distance of 400 m from the mouth of the estuary, the highest Cd concentration was found at station A, while at a distance of 800 m from the mouth of the estuary, the lowest concentration was found at the same station.

On the surface sediment, the highest Cu concentration was at a distance of 1600 m from the mouth of the estuary precisely at station B, and the lowest was at the distance of 400 m from the mouth of the estuary at the B station.

On the surface sediment, the highest concentration of was located at a location with a distance of 1600 m from the mouth of the estuary (precisely at station B), and the lowest concentration of Zn was at a distance of 400 m from the mouth of the estuary (precisely at station B).

The distribution of Pb, Cd, Cu and Zn content in sediments depends on the level of contaminants in the water undergoing the process of adsorption with suspended particles and undergoing a process of precipitation. The process of settling a compound was very dependent on the flow velocity and the size of the particles which absorb the Pb, Cd, Cu, and Zn compounds. With a weak flow rate and large particle size, the deposition process will take place with a fast time and with a short distance from the source of the contaminants, and when the flow velocity was strong, the deposition process will be longer and farther from the source of the contaminants.

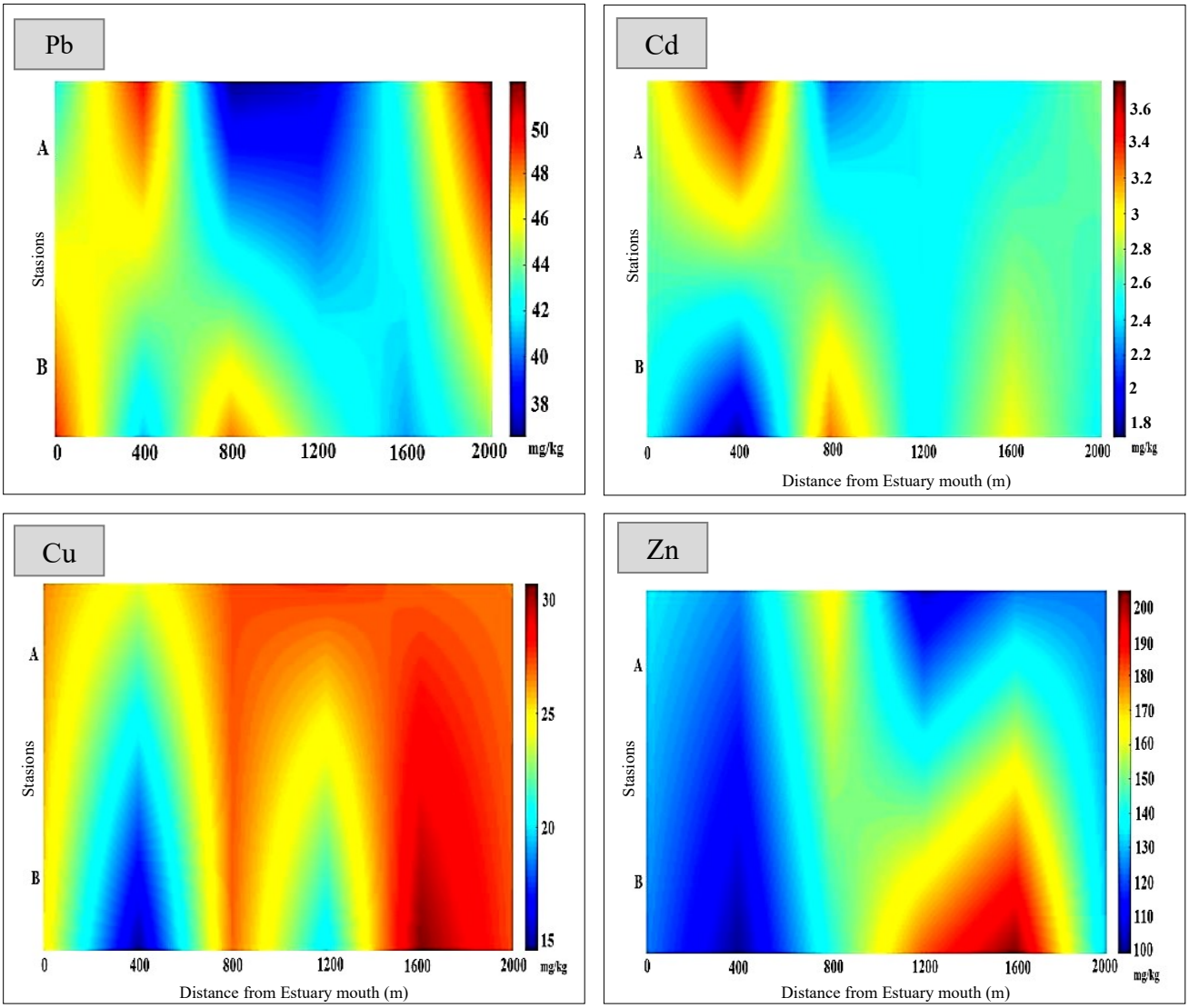

Fig.4. Spatial distributions of Pb, Cd, Cu, and Zn in surface sediment (2-Dimensional)

4 Conclusion

Heavy metals sequence from the highest pollution level in the water were: Zn > Pb > Cu > Cd, and in the sediment were: Cd > Pb > Zn > Cu. Pb, Cd, Cu, and Zn had a tendency to be in the sediment compared to the water (ACI = 99.69% – 99.89%; DTI = 0.109% – 0.309%), slightly mobile (log K_{oc} = 3.11 – 3,58), and hydrophobic (log K_{ow} = 3.35 – 3.87). Pb and Cd showed significantly different concentrations in the water columns (surface/midst/base) (p<0.05), in contrast to Cu and Zn. Pb, Cd, Cu, and Zn had insignificant concentration difference based on zone division from estuary mouth, both in the water and the sediment.

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