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Research Article

Multivariate Analysis on Heavy Metals Distribution in Tropical Reservoir

[1]Nor Bakhiah Baharim, [1]Zulkifli Yusop, [2]Wan Zakaria Wan Muhd Tahir, [3]Ismail Yusoff, [1]Muhamad Askari, [4]Zainudin Othman, [5]Mohamed Roseli Zainal Abidin
[1]Institute of Environmental and Water Resource Management, Universiti Teknologi Malaysia, 81310 Skudai, Johor
[2]Isotope and Tracer Application Group (e-TAG), Division of Environment and Waste Management, Malaysian Nuclear Agency (Nuclear Malaysia), 43000 Bangi, Kajang, Selangor, Malaysia
[3]Department of Geology, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia
[4]Department of Geography and Environment, Sultan Idris University of Education, 35900 Tanjung Malim, Perak, Malaysia
[5]Humid Tropics Centre Kuala Lumpur (HTCKL), No 2 Jalan Ledang off Jalan Duta, 50480, Kuala Lumpur, Malaysia

Abstract: Chemical properties of bottom sediment in manmade reservoir were analyzed. Principal component analysis and factor analysis were conducted to differentiate the sources of heavy metals. The mean concentrations of heavy metals decrease in the following order: Mn>Pb>As>Zn>Cr>Cu. The spatial distribution of heavy metals shows that oil palm plantation and modern agricultural activities influence heavy metal distribution. Heavy metal contents were higher in the west wing and could be associated with micronutrient fertilizer from oil palm plantation with remarkable increases, especially for Zn, Cu and Mn.

Keywords: Agricultural activities, heavy metals, principal component analysis

INTRODUCTION

Heavy metal contamination in sediments could have long-term implications on human health because surface water is the main source of water supply. Heavy metal contamination can cause toxicity as well as harm the aquatic environment (Ghrefat and Yusuf, 2006; Çevik *et al*., 2009; Tabari *et al*., 2010; Chen *et al*., 2007). The accumulation of heavy metal in reservoirs is controlled by complex physical and chemical adsorption mechanisms that are triggered by natural processes or human activities (Spencer and MacLeod, 2002; Abraham, 1998; Ghrefat and Yusuf, 2006; Çevik *et al*., 2009). Anthropogenic sources of heavy metals in sediments mainly come from agricultural activities, urbanization, industrialization and mining (Micó *et al*., 2006; Dragović *et al*., 2008; Cai *et al*., 2012; Krami *et al*., 2013).

Previous studies in Wadi Al-Arab Dam, Jordan and Seydan Dam, Turkey show that the application of fertilizer and pesticide in agricultural activities is the main source of anthropogenic input, particularly Zn and Cd (Ghrefat and Yusuf, 2006; Çevik *et al*., 2009). Studies on risk assessment and ecological risk of heavy metals in reservoir sediment have been conducted by previous researchers (Çevik *et al*., 2009; Ghrefat *et al*., 2011; Dou *et al*., 2012; Prasanna *et al*., 2012).

Two main rivers flow into the reservoirs, namely, Sembrong River and Marpo River. As heavy metal pollution poses a serious threat to human health and ecosystems, studying sediment quality has become a major concern to many researchers. This study aims to address this issue and achieve the following objectives:

- To determine the chemical properties in bottom sediment cores
- To determine the spatial distribution of heavy metals in Sembrong Reservoir.

MATERIALS AND METHODS

Study area: Sembrong Reservoir is located in the southern part of Peninsular Malaysia between latitudes 3°26′42″ to 3°26′42″ N and longitudes 102°54′18″ to 102°55′54″ E (Fig. 1). The reservoir area is approximately 77.5 ha with a storage capacity of approximately 24.8 million m^3. Geologically, the study area is underlain by Layang Layang Formation and comprises tertiary sediment. Layang Layang Formation consists of partly consolidated gravel and sand, soft shale, often carbonaceous seams of low-grade coal and

Corresponding Author: Zulkifli Yusop, Water Research Alliance, Level 2, Block C07, Faculty of Civil Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Tel.: 6075531579

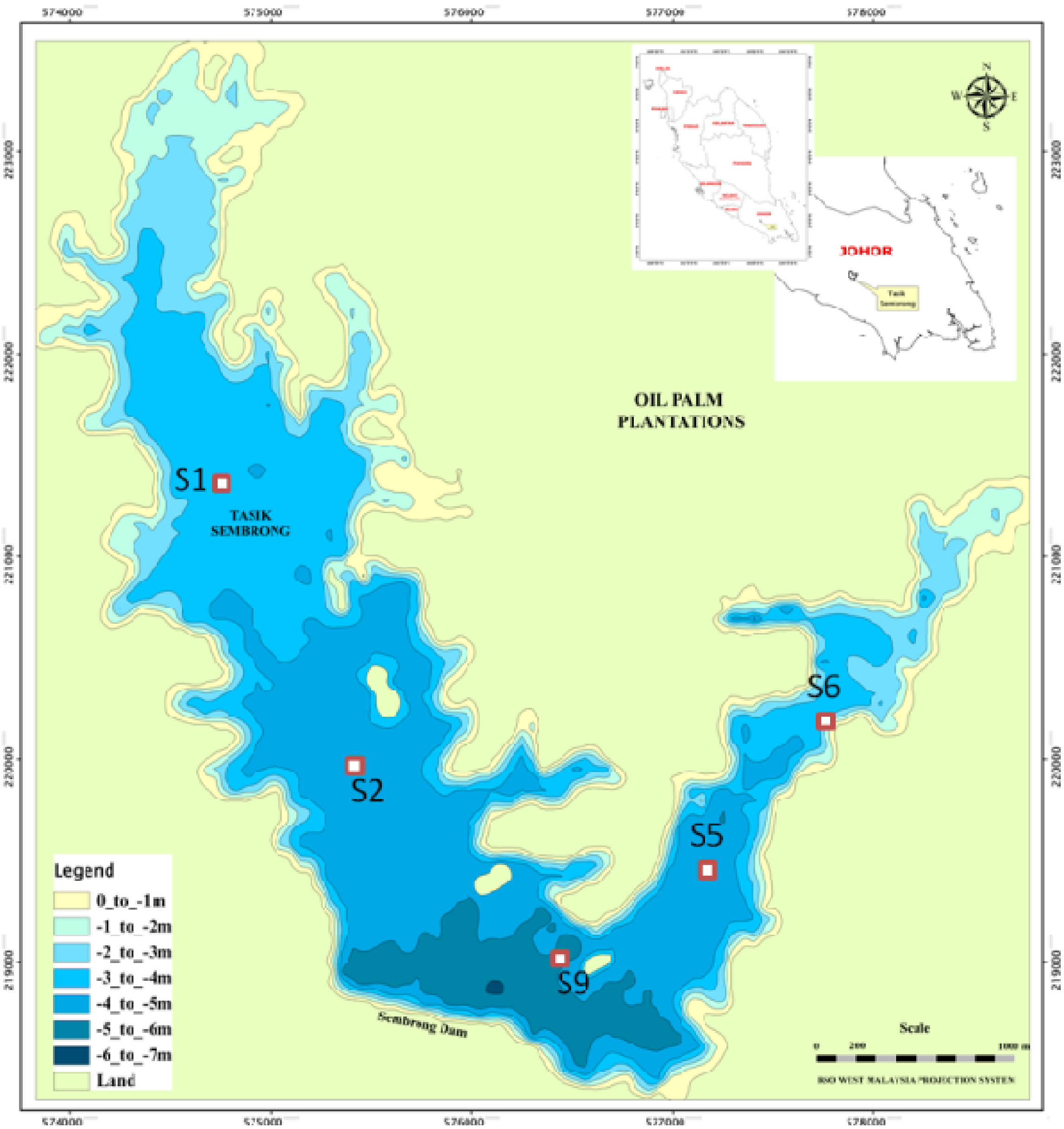

Fig. 1: Bathymetry map of Sembrong Reservoir and locations of the core sediment sampling

rare calcareous shale (Hutchison *et al*., 2009). This reservoir was constructed in 1984 and was originally designed for flood mitigation, but has been used for water supply since 1997. The land use map of the reservoir catchment has been frequently updated by the Department of Agriculture Malaysia since 1966 (Table 1). Currently, land use within the catchment is mainly oil palm plantation (approximately 60%), rubber (5%), commercial/residential (2%), mixed horticulture (2%), idle grassland (2%), reservoir (6%), pasture/modern agriculture (17%), secondary forest (2%), natural forest (2%) and swamp forest (2%).

Sampling: Five bottom sediment cores were collected at different stations in Sembrong Reservoir by using the UM core sampler. This core sampler was designed for bottom lake sediment and equipped with two transparent acrylic tubes (Gharibreza *et al*., 2013b, c; Gharibreza *et al*., 2013a). The sampling stations were chosen carefully based on the bathymetry map. Bottom sediment cores were obtained from the deepest possible depth to ensure that the sediment contains the finest grains of clay (Hakanson, 1980). After sampling, the sediment samples were frozen at -10°C before being sliced at 2-cm intervals. The samples were dried at 80°C and weighted.

The acid digestion procedure was conducted by using the Multiwave 3000 oven and following Method 3052. For each slice, a 0.25 g powder sample was mixed with acid mixture that contains 9 mL HNO_3,

Table 1: Changes in land use compositions in Sembrong Reservoir from 1966 to 2010

	Percentage									
Land use	1966	1974	1984	1990	1997	2000	2002	2004	2008	2010
Mixed horticulture		1	0	0	2	2	2	2	2	2
Rubber	31	34	36	36	18	17	17	5	5	5
Oil palm	0	6	8	8	31	38	42	60	60	60
Pasture/agriculture	2	10	13	13	14	14	14	17	17	17
Idle grassland	13	1	1	1	2	5	2	1	2	2
Newly cleared areas	3	2	7	7	1	2	2	1	1	1
Forest	23	29	29	20	2	2	2	2	2	2
Swamp forest	16	14	11	11	6	6	5	2	2	2
Secondary forest	3	3	2	2	16	6	6	4	4	4
Pond/water body			3	3	6	6	6	6	6	6
Residential	1	1	–	–	2	2	2	2	2	2

2 mL HCl and 3 mL HF. The samples were then completely digested by adding 12 mL of saturated boric acid solution (H_3BO_4). The chemical properties were determined by using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

RESULTS

Sediment core quality: The descriptive statistics of chemical properties are shown in Table 2. The values range from 26, 212 mg/kg to 227, 121 mg/kg for Al, from 2, 071.6 mg/kg to 61,743.9 mg/kg for Fe, from 2, 992.6 mg/kg to 10, 718.2 mg/kg for K, from 682.6 mg/kg to 3,116.3 mg/kg for Na, from 539.7 mg/kg to 1,172.3 mg/kg for Mg and from 64.4 mg/kg to 2,995 mg/kg for Ca. For heavy metals, the values range from 0.18 mg/kg to 21.18 mg/kg for Cu, from 8.90 mg/kg to 73.91 mg/kg for Cr, from 15.89 mg/kg to 538.50 mg/kg for Mn, from 16.88 mg/kg to 63.50 mg/kg for Pb and from 7.50 mg/kg to 111.34 mg/kg for Zn. The mean concentrations of heavy metals decreased in the following order: Mn>Pb>As>Zn>Cr>Cu.

Multivariate analysis: Principal component analysis was applied to elucidate the potential sources of heavy metals in the reservoir. The results are shown in Table 3. Two main components with eigenvalues of >1 were selected. The loadings of the first two principal components of heavy metals are shown in Fig. 2. Positive correlations are observed among Cu, Cr, Mn, Pb and Zn, with a total variance of 60.47% (Factor 1). This factor indicates a strong association of Cu, Cr, Mn, Pb and Zn, with *r* values that range from 0.73 to 0.94. Factor 2 accounts for 21.56% of the total variance and comprises As only. A weak correlation between Factors 1 and 2 suggests that both factors have different sources.

In addition, a dendogram shows the similarities and dissimilarities among heavy metals divided into two classes (Fig. 3). Class 1 consists of the element As only and Class 2 represents the strong correlations between Cu, Cr, Mn, Pb and Zn. Class 2 is divided into two clusters, with the first cluster comprising Cu and Mn and the second cluster comprising Cr, Pb and Zn.

Table 2: Descriptive statistics of heavy metal concentrations in the bottom sediment in Sembrong Dam

Metal	Station	Min	Max	Mean
As	2	16.39	39.58	26.66
	6	18.54	65.41	24.68
	1	10.58	61.13	28.43
	5	28.93	61.06	44.98
	9	44.21	67.80	54.99
Cr	2	62.95	50.71	39.63
	6	9.95	36.60	13.20
	1	37.83	73.91	51.50
	5	24.36	13.17	8.26
	9	8.90	23.87	15.86
Cu	2	9.43	12.24	10.93
	6	2.21	17.20	4.20
	1	12.40	21.18	16.57
	5	0.85	9.26	2.96
	9	0.18	10.55	3.51
Mn	2	81.29	174.27	112.51
	6	18.74	109.32	29.84
	1	145.56	538.50	308.18
	5	15.89	98.55	35.07
	9	28.02	79.87	44.31
Pb	2	38.42	63.50	49.72
	6	16.88	51.21	21.45
	1	33.55	55.32	44.21
	5	23.99	51.41	37.18
	9	36.21	57.00	43.04
Zn	2	44.39	66.22	52.51
	6	9.35	111.34	17.75
	1	34.92	55.15	45.77
	5	7.50	90.96	21.61
	9	10.50	64.55	23.26

Both clusters are linked to each other and appear to be associated with natural and anthropogenic sources. Cu and Mn are associated with each other because both have a strong bond with organic matter (Loska and Wiechuła, 2003; Bhuiyan *et al*., 2010). In addition, Mn is subject to oxidation that triggers mobilization of Cu from the sediment. Therefore, the increments of Cu in sediments are proportional with Mn. Geologically, Cr, Pb and Zn primarily come from lithogenic origins, especially from chalcophylic nature. As such, Cr, Pb and Zn might be derived from natural sources and enriched by human-induced sources. The relationships between Cr, Pb and Zn suggest that these heavy metals originated from similar sources and were deposited together.

Multivariate analyses have successfully distinguished the sources of heavy metals in the

Table 3: Factor analysis of heavy metal concentrations for bottom sediment at Sembrong Reservoir

Component	Total	% of variance	Cumulative %	Factor 1	Factor 2
Cu	4.103	58.612	58.612	0.945	-0.186
Cr	1.306	18.662	77.274	0.866	-0.298
Zn	0.882	12.597	89.871	0.853	0.151
Mn	0.419	5.993	95.863	0.842	-0.144
Fe	0.155	2.219	98.082	0.743	0.249
Pb	0.088	1.261	99.343	0.687	0.340
As	0.046	0.657	100.000	0.009	0.981

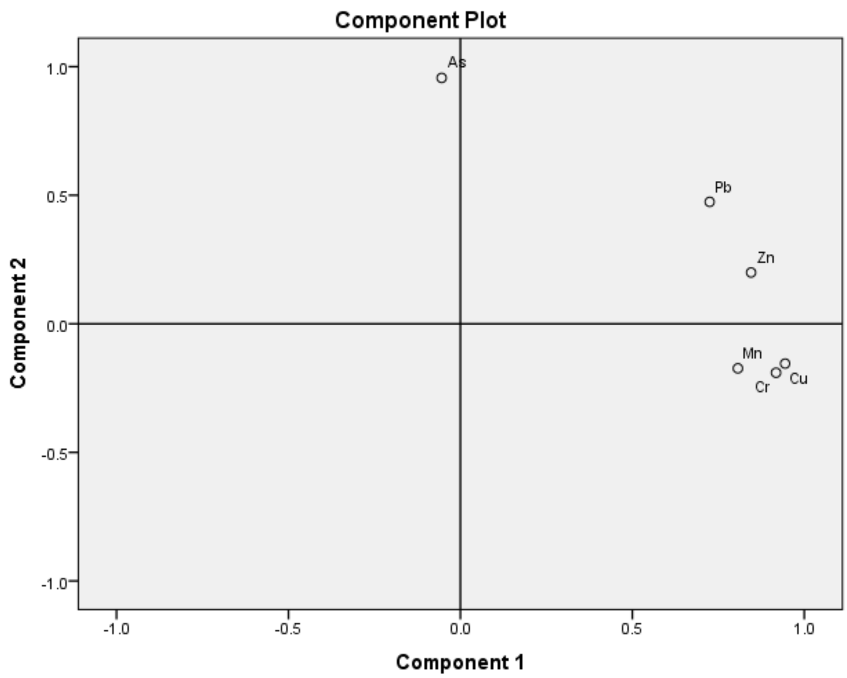

Fig. 2: Loading plot of the principal component of heavy metals in Sembrong Reservoir

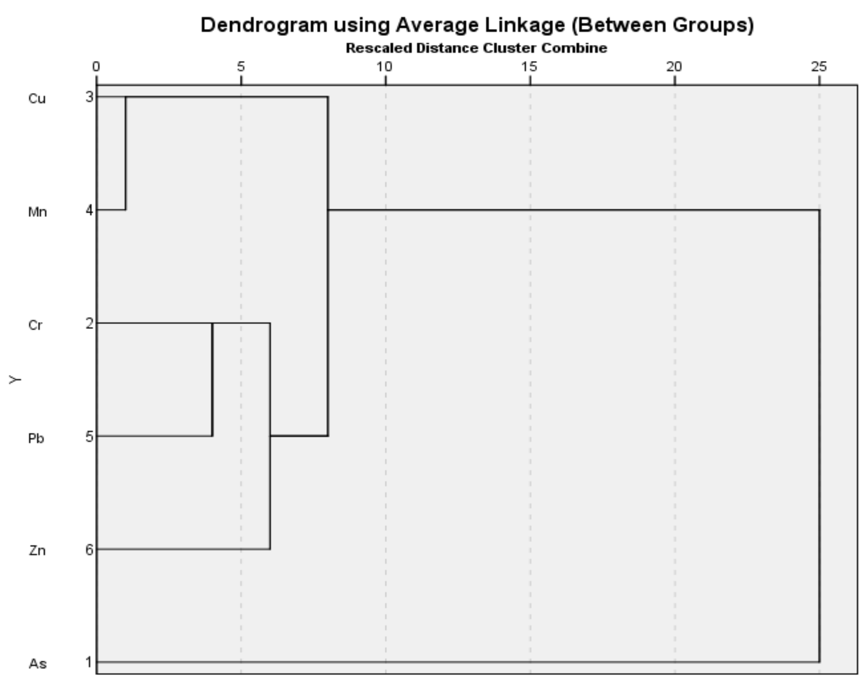

Fig. 3: Dendrogram obtained by hierarchical clustering of heavy metals

reservoir. Cu, Cr, Mn, Pb and Zn can be classified as an "anthropogenic factor" that most likely originates from micronutrients in chemical fertilizer (Micó *et al*., 2006; Sun *et al*., 2013; Dou *et al*., 2012; Huang *et al*., 2007). Chemical fertilizer is extensively used in agricultural cropss to replenish soil quality. The application of micronutrient fertilizers, such as borate, copper and zinc sulfates, especially in oil palm plantation (Sabri, 2009; FOA, 2004) might be responsible for the presence of heavy metals in the northwest and southwest of the reservoir. By contrast, Cai *et al*. (2012) and Dou *et al*. (2012) explained that As could also be associated with other heavy metals, such as Zn and Cd, that originated from phosphorous fertilizer. However, the result indicates that Cd is absent and As did not associate with other heavy metals. Therefore, As may originate from a single source, most likely from geological substrates.

CONCLUSION AND RECOMMENDATION

Identifying and quantifying heavy metals are important for environmental studies. The results indicate that agricultural activities have contributed to heavy metal influxes at Sembrong Reservoir. The rapid expansion of the area that surrounds the oil palm plantation seems to cause high heavy metal contents in sediment, especially in the eastern part of the reservoir. The additional sources of heavy metals, especially Mn, Cu, Cr, Zn and Pb, most likely come from micronutrient fertilizer. The distribution of sediment particles and chemical properties in the reservoir is influenced by the physical mixing process.

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