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Pollution Assessment of Various Heavy Metals in the Surface Sediment of Kendari Bay, Indonesia

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ABSTRACT

The concentration and pollution level of heavy metals in the surface sediments of Kendari Bay, Indonesia were measured. Sediments samples from 25 sites, ranging from the inshore (Wanggu River) to the offshore regions of the bay, were analysed for metal concentrations (i.e., Mn, Fe, Co, Ni, Cu and Zn), sediment type and TOC. The results demonstrate that the heavy metal Fe had the highest concentrations (1100 to 29800 µg/g) followed by Mn (34.39 to 399.59 µg/g), Zn (2.58 to 129.70 µg/g), Ni (1.14 to 15.34 µg/g), Cu (0.6 to 15.81 µg/g), and Co (0.24 to 7.33 µg/g). Moreover, results of both Pearson correlation analysis and PCA suggest the similar distinctiveness of Fe, Co and Ni in 25 sampling sites. The measurement results of index of geoaccumulation (I_{geo}) suggest that the Kendari Bay surface sediment is considered an unpolluted area for each of the heavy metals investigated in this study.

INTRODUCTION

The coastal environment is a complex system that is likely to change as a result of various biogeochemical mechanisms inside the system. Such a coastal zone should be preserved because it plays an important role for human life. Due to the rapid industrial development in the coastal zone, pollutants (including heavy metals) are introduced regularly all over the world (Romano et al. 2004). The behaviour of heavy metals within aquatic systems has been an issue of increasing concern in environmental studies over the past few years because of the metals' ecotoxicity features, persistence and bioaccumulation as well as biomagnification in marine systems (Tam & Wong 2000, Wang et al. 2015). As such, heavy metals represent a potential hazard to aquatic organisms and human health.

The transport of heavy metals in both estuaries and coastal regions are subject to various influences, including sewage effluents, industrial discharge, urban and agricultural runoff, atmospheric deposition, and the combined inputs from the rivers (Neto et al. 2006). Such inclusion has led to contamination of coastal environments by heavy metals (Liu et al. 2003). When the metals are released into the coastal environment, they are transferred to the sediments via adsorption onto suspended matter and successive sedimentation (Jonathan et al. 2004). Therefore, coastal sediment serves as a repository for heavy metal contaminants, and so the concentrations of heavy metals found in the sediment are far greater than those of the overlying water column.

Sediment is a mixture of materials comprising detritus, clay mineral, silicate, and inorganic and organic particles and is relatively heterogenous in terms of its physical, chemical and biological characteristics (Wu et al. 2011). Sediments play an important role in the remobilization of metals to the aquatic environment (Rosales-Hoz et al. 2007). The accumulation of heavy metals in the global marine sediment system has been detected over the last few decades. Because the addition of heavy metals occur continuously in the marine system, coastal sediment can serve as a good recorder of the anthropogenic activities which cause heavy metal pollution in the coastal environments (Guevara et al. 2005).

Kendari bay is a coastal zone located in Kendari city, in the province of southeast Sulawesi, Indonesia. This bay has attracted increased human activity over the years, and industries such as tourism, transportation, fishing and shipping thrive along the coastal region and in the city. Three ports, which are located inside the bay (Ferry, Perikanan Samudera and Nusantara), may influence the concentration of metals in the water and sediments of the bay into which the Wanggu River flows. Nevertheless, to date, research into the heavy metal distribution in this location is notably limited (Armid et al. 2014). In view of that, it is imperative to identify the geochemical distribution and pollution status of heavy metals in the sediment of Kendari bay with the intention of controlling anthropogenic sources of pollution, in order to manage the quality of water in this region and to ensure that the metal concentrations are below harmful levels. This study was undertaken to evaluate the concentration of the heavy metals Mn, Fe, Co, Ni, Cu and Zn in the surface coastal sediment of Kendari bay in order to observe their prevalence compared to other surrounding coastal regions in the world. Additionally, the index of geoaccumulation (I_{geo}) was estimated for each of the elements analysed.

MATERIALS AND METHODS

Sampling: Surface sediment samples were collected during October 2014 using an Ekman grab sampler from 25 sampling sites ranging from the lower reaches of the Wanggu River to the offshore region of Kendari Bay (Fig. 1). The points are clustered into 6 sampling regions, including Wanggu River (1, 2, 3, 4 and 5), estuary (6, 7, 8, 9 and 10), inner bay (11, 12, 13, 14 and 15), ports (16, 17, 18, 19, 20 and 21), outer bay (22 and 23) and offshore (24 and 25). The geographic position of each sampling site was recorded by a Global Positioning System (Garmin Montana 680, Taiwan). The collected sediment was carefully removed from the middle of the sediment sampler using a plastic spatula. To prevent metal contamination, the samples were directly inserted into plastic bags and kept frozen until analysis.

Sediment treatment and analysis: The sediments were analysed for grain size, total organic carbon (TOC) and heavy metal concentrations. Grain size analysis was performed for sand, silt and clay distributions using a sieving method for the coarse fractions, and a particle size analyser (a SediGraph III 5120) for the fine fractions. The TOC analysis was carried out using a Carlo Erba NA-1500 Analyser. For heavy metals analysis, all samples were dried at room temperature until each reached a constant weight, and were then disaggregated in an agate mortar prior to chemical treatments. Concentration of the heavy metals Mn, Fe, Co, Ni, Cu and Zn were determined by total digestion of sediments in HNO_3/HF and analysed by inductively coupled plasma mass spectrometry (ICP-MS) (Thermo Scientific™ XSERIES 2 ICP-MS, Germany). Each measurement of heavy metals was run in triplicate using SPEX XSTC-331 as a multi-elemental standard solution. The concentration of metals is reported in µg/g dry weight. A blank was prepared using the same amount of acid in each digestion process. The detection limits were found to be 25.4, 116.6, 4.1, 3.3, 7.3 and 112.9 ng/g dry weight for Mn, Fe, Co, Ni, Cu and Zn, respectively. The accuracy of the measurement was assessed using the marine sediment reference material NIES CRM No. 12 from Environment Agency of National Institute for Environmental Studies, Japan, and found the recoveries to be 96, 97, 93, 98, 93 and 101% for Mn, Fe, Co, Ni, Cu and Zn, respectively. Pearson's correlation coefficients were utilized to identify the relationships among heavy metal concentrations or within TOC values. The relationship between heavy metal distributions and sampling points was statistically interpreted by principal components analysis (PCA) and hierarchical clustering analysis (HCA) using the computer program MINITAB 17.1.0.0 (Minitab Inc., State College, Pennsylvania, USA).

RESULTS AND DISCUSSION

Sediment type and TOC value: The type and TOC of the surface sediments are presented in Table 1. The Wanggu River sediments are predominantly silt, followed by sandy silt typically found in the estuary and inner bay. The surface sediment in Perikanan Samudera Port (sampling sites 16 and 17) is mainly composed of sandy silt, possibly derived from the nearby inner bay region; this then gradually transforms into the silty sand type of sediment found in Ferry and Nusantara Ports. Finally, the outer bay and the offshore regions are predominantly silty sand and sand, respectively. Therefore, the types of surface sediments contained in Kendari bay vary depending on the location of the sample and in general exhibit a gradual change from finer particles (silt) in the Wanggu River to coarser particles (sand) in the offshore region. Fine sediments that are typical of those found in the Wanggu River samples are likely a result of the input of freshwater containing finer particles which settle out upon reduction of the flow rate of the river and the wind currents (Raj & Jayaprakash 2008). The estuary and the inner bay regions are protected from wave and tidal current activities; hence, they accumulate a relatively similar type of sediment (sandy silt). Nonetheless, there is an indication of a consistently stable depositional marine environment in the Kendari bay, given the similarity of sediment types found in the Wanggu River, estuary and inner bay (silt), the Wanggu River, estuary, inner bay and ports (sandy silt) and also the ports and outer bay (silty sand). In addition, the direct influence of either intense seawater dynamics or materials coming from the Banda Sea might wash out finer particles, and so the offshore region is dominated by sand. It has to be noted that such sediment type transformation from the Wanggu River to the offshore region is in agreement with the variation of TOC values, whereby the TOCs of finer particles are higher than those of coarser particles. The TOC distribution recorded in the Kendari bay

Table 1: Types, TOC and heavy metal concentrations in the surface sediments of Kendari bay.

Sampling site	Sample region	Latitude S	Longitude E	Type of sediment	TOC (%)	Concentration (µg/g)					
						Mn	Fe	Co	Ni	Cu	Zn
1	Wanggu River	-3.9869	122.5211	Silt	2.63	94.15	18,900	5.11	14.86	6.96	67.50
2	Wanggu River	-3.9838	122.5238	Silt	2.57	101.45	22,100	7.33	13.09	8.61	60.58
3	Wanggu River	-3.9791	122.5263	Silt	2.57	99.89	28,600	6.48	13.86	7.49	59.55
4	Wanggu River	-3.9796	122.5310	Silt	2.64	100.29	29,800	6.51	15.34	7.21	65.28
5	Wanggu River	-3.9781	122.5336	Sandy Silt	2.19	98.03	23,000	6.24	13.03	6.66	64.91
6	Estuary	-3.9697	122.5360	Silt	2.59	95.06	8,700	1.43	10.96	2.80	49.70
7	Estuary	-3.9829	122.5399	Sandy Silt	2.20	93.53	6,700	1.53	7.09	1.98	50.53
8	Estuary	-3.9743	122.5379	Sandy Silt	2.19	92.71	7,100	1.48	9.22	2.15	46.69
9	Estuary	-3.9863	122.5526	Sandy Silt	2.17	92.93	6,900	1.42	9.98	2.10	45.33
10	Estuary	-3.9871	122.5436	Sandy Silt	2.15	91.26	8,100	1.38	11.23	1.95	51.22
11	Inner bay	-3.9786	122.5511	Sandy Silt	2.16	93.16	6,000	1.36	7.32	1.60	11.29
12	Inner bay	-3.9734	122.5466	Silt	2.65	95.72	6,800	1.36	7.20	1.76	11.37
13	Inner bay	-3.9718	122.5577	Sandy Silt	2.20	87.64	8,300	1.37	7.44	1.82	13.75
14	Inner bay	-3.9776	122.5604	Sandy Silt	2.17	80.21	7,200	1.35	6.94	1.77	19.23
15	Inner bay	-3.9729	122.5661	Sandy Silt	2.15	81.66	6,100	1.33	7.11	1.73	11.34
16	Port	-3.9801	122.5703	Sandy Silt	2.13	61.39	11,100	2.89	12.87	15.81	129.00
17	Port	-3.9798	122.5751	Sandy Silt	2.17	65.86	11,500	2.89	12.37	15.74	129.70
18	Port	-3.9737	122.5757	Sandy Silt	2.16	398.69	21,700	5.15	14.37	7.91	55.20
19	Port	-3.9738	122.5787	Silty Sand	1.71	399.59	21,800	5.33	14.60	8.28	54.89
20	Port	-3.9746	122.5827	Sandy Silt	2.13	357.67	19,800	4.30	12.21	7.03	42.46
21	Port	-3.9756	122.5870	Silty Sand	1.73	352.32	18,200	4.17	12.22	6.84	41.64
22	Outer bay	-3.9796	122.5962	Silty Sand	1.72	56.55	4,700	1.23	3.49	2.68	9.56
23	Outer bay	-3.9750	122.6032	Silty Sand	1.79	53.79	5,600	0.79	4.10	3.11	8.73
24	Offshore	-3.9411	122.6569	sand	1.31	34.39	1,100	0.24	1.15	0.62	2.65
25	Offshore	-3.9453	122.6632	sand	1.24	40.49	1,300	0.24	1.14	0.60	2.58

Table 2: Concentrations of heavy metals in Kendari bay sediments (this study) compared with those from other locations.

References	Location	Mn (µg/g)	Fe (µg/g)	Co (µg/g)	Ni (µg/g)	Cu (µg/g)	Zn (µg/g)
Neto et al. (2000)	Jurujuba Sound, Southeast Brazil	10-414	1,000-21,250	-	15-79	5-213	15-337
Jonathan et al. (2004)	Gulf of Mannar, southeast coast of India	122-640	4,100-29,400	9-29	14-58	34-110	39-162
Buccolieri et al. (2006)	Taranto Gulf (Southern Italy)	893	31,566	-	53.3	47.4	102.3
Raj & Jayaprakash (2008)	Bay of Bengal, southeast coast of India	284-460	17,000-37,000	5.8-11.8	19.8-53.4	385-657	71.3-201
Fang et al. (2009)	East China Sea	484	21,000	-	26	15	60
Pereira et al. (2015)	Todos os Santos Bay, Brazil	21.03-1197.30	1,781.43-12,184.67	1.06-3.09	5.09-8.02	0.94-7.75	11.81-40.10
Obhođaš & Valković (2010)	The Croatian Adriatic coast	14.9-745.0	25.0-4280.0	-	5.8-71.1	5.2-58.2	10.8-109.8
This study	Kendari Bay, Indonesia	34.39-399.59	1,100-29,800	0.24-7.33	1.14-15.34	0.60-15.81	2.58-129.70

surface sediments varies from 1.24% to 2.64% with an average of 2.13%. The record of high TOC value, which is preserved in fine-grained sediments (as with the Wanggu River sediments in this study), has been clearly investigated in previous studies (Salomons & Forstner 1984, Caccia et al. 2003, Cho et al. 1999, Wu et al. 2011); these sediments are mostly a result of terrigenous material inputs from the adjacent land mass, industrial effluents and the deposition of organic debris. TOC has an important role in the geochemical cycles of elements accumulated in sediments

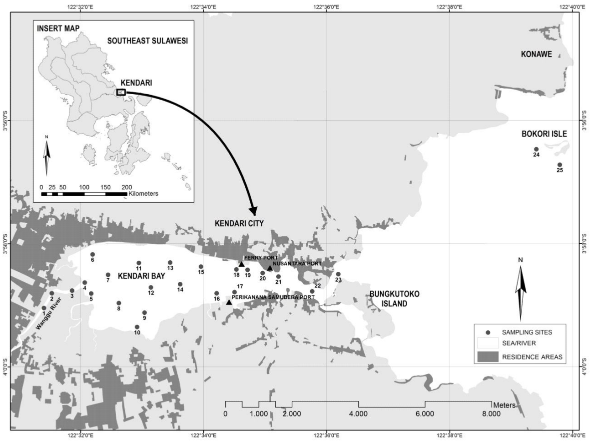

Fig. 1: Location of Kendari bay and the 25 sampling sites.

and it is possible to use TOC as an index of depositional and sedimentary processes (Seralathan et al. 1993).

Trends in the heavy metal concentrations in surface sediment: Table 1 presents the heavy metal concentrations in surface sediments around Kendari bay. Fe has the highest concentrations (1100 to 29800 µg/g), followed by Mn (34.39 to 399.59 µg/g), Zn (2.58 to 129.70 µg/g), Ni (1.14 to 15.34 µg/g), Cu (0.6 to 15.81 µg/g), and Co (0.24 to 7.33 µg/g). Fig. 2 summarizes the average concentrations of heavy metals in each sampling region. In general, heavy metal concentrations in the sediments displayed similar trends in distribution, where their concentrations decreased from Wanggu River towards the inner bay, then they rose significantly in the samples coming from the port regions and after that all the concentrations fall back to the offshore region. Among these metals, the highest concentrations of Fe, Co and Ni were observed in the Wanggu River sediments (Fig. 2), while the concentrations of Mn (sampling sites 18 to 21), Zn (sampling sites 16 and 17) and Cu (sampling sites 16 and 17) were found to be highest in the port sediments (Table 1).

The highest concentration of heavy metals (Fe, Co and Ni) in the Wanggu River may be a result of anthropogenic inputs such as untreated sewage from mining and industrial activities, in addition to agricultural runoff. Mining activities in the Province of Southeast Sulawesi have increased significantly in the last decade. It is noted that there are recently 136 ore mining companies operating in North Konawe, Konawe and South Konawe Regencies (CBSSS 2015), where the entireties of those districts are crossed by the water flow of the Wanggu River. The waste generated from mining activities can enter the Wanggu River directly or indirectly, and thereby increase the anthropogenic accumulation of heavy metals in the water and sediment systems of the river (Armid et al. 2014). In addition, increasing proportions of finer-grained sediment particles (associated with the higher TOC values) in Wanggu River sediments may provide greater surface area for sorption of chemical pollutants, resulting in the enrichment of heavy metals in these sediments.

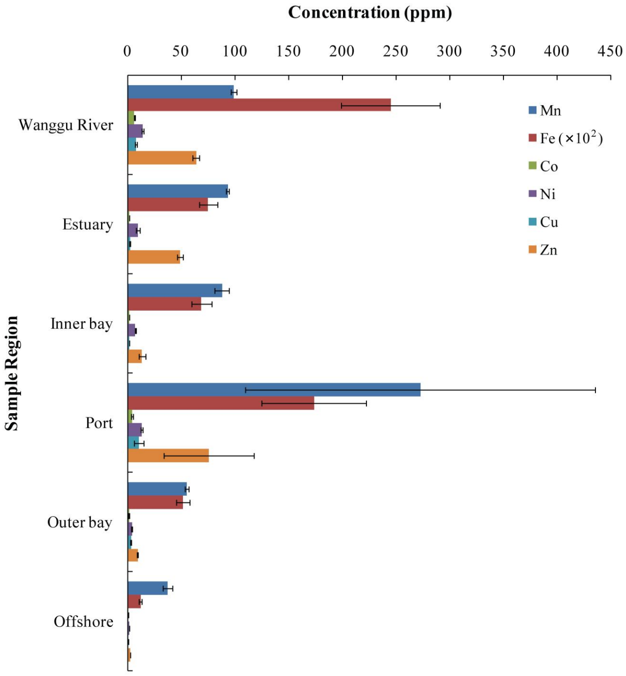

Fig. 2: Concentrations of heavy metals based by sample region in Kendari bay.

Fig. 2 further shows lower concentrations of heavy metals in the Kendari bay estuary, which is a region that is populated mostly by mangroves. The existence of mangroves may cause phytoremediation in the estuarine environment, i.e., the translocation of contaminants (including heavy metals) from soils, sediments, and surrounding waters into the body tissues of the mangroves. Such a process is likely responsible for the lower heavy metal concentrations in the estuary system (MacFarlane et al. 2007, Weis & Weis 2004). Several studies have been performed to evaluate the potential of mangrove ecosystems in phytoremediation of metals, for example, phytoremediation of Cu, Cd, Ni, Mn, Cr, Zn, Fe and Pb in the sediments of Alibag, West coast of India (Pahalawattaarachchi et al. 2009).

In the inner region of the bay, the heavy metal concentrations are even lower than those of the estuary, measuring 6% for Mn, 8% (Fe), 7% (Co), 26% (Ni), 21% (Cu) and 72% (Zn) (Fig. 2). This may be explained by the tidal currents and wave action in this region which reduce the accumulation of heavy metals in the surface sediments. In addition,

Table 3: Index of geoaccumulation (I_{geo}) of heavy metals in the surface sediments of Kendari Bay and pollution status.

Sampling site	Sample Region	Index of geoaccumulation						Pollution status
		Mn	Fe	Co	Ni	Cu	Zn	
1	Wanggu River	-3.76	-1.91	-2.48	-2.78	-3.28	-1.08	Unpolluted
2	Wanggu River	-3.65	-1.68	-1.96	-2.96	-2.97	-1.23	Unpolluted
3	Wanggu River	-3.67	-1.31	-2.14	-2.88	-3.17	-1.26	Unpolluted
4	Wanggu River	-3.67	-1.25	-2.13	-2.73	-3.23	-1.13	Unpolluted
5	Wanggu River	-3.70	-1.62	-2.19	-2.97	-3.34	-1.13	Unpolluted
6	Estuary	-3.75	-3.02	-4.32	-3.22	-4.59	-1.52	Unpolluted
7	Estuary	-3.80	-3.13	-4.22	-3.18	-5.11	-1.48	Unpolluted
8	Estuary	-3.78	-3.32	-4.27	-3.47	-4.97	-1.61	Unpolluted
9	Estuary	-3.78	-3.36	-4.33	-3.35	-5.01	-1.65	Unpolluted
10	Estuary	-3.77	-3.40	-4.37	-3.85	-5.09	-1.50	Unpolluted
11	Inner bay	-3.77	-3.56	-4.39	-3.80	-5.40	-3.66	Unpolluted
12	Inner bay	-3.74	-3.38	-4.39	-3.83	-5.26	-3.65	Unpolluted
13	Inner bay	-3.86	-3.09	-4.38	-3.78	-5.21	-3.37	Unpolluted
14	Inner bay	-3.99	-3.30	-4.40	-3.88	-5.25	-2.89	Unpolluted
15	Inner bay	-3.96	-3.54	-4.42	-3.84	-5.29	-3.65	Unpolluted
16	Port	-4.38	-2.67	-3.30	-2.99	-2.09	-0.14	Unpolluted
17	Port	-4.28	-2.62	-3.30	-3.04	-2.10	-0.14	Unpolluted
18	Port	-1.68	-1.71	-2.47	-2.83	-3.09	-1.37	Unpolluted
19	Port	-1.67	-1.70	-2.42	-2.80	-3.03	-1.38	Unpolluted
20	Port	-1.83	-1.84	-2.73	-3.06	-3.26	-1.75	Unpolluted
21	Port	-1.86	-1.96	-2.77	-3.06	-3.30	-1.78	Unpolluted
22	Outer bay	-4.49	-3.91	-4.53	-4.87	-4.65	-3.90	Unpolluted
23	Outer bay	-4.57	-3.66	-5.17	-4.64	-4.44	-4.03	Unpolluted
24	Offshore	-5.21	-6.01	-6.91	-6.48	-6.76	-5.75	Unpolluted
25	Offshore	-4.98	-5.77	-6.88	-6.48	-6.82	-5.79	Unpolluted

several chemical processes, including adsorption-desorption, complex formation, precipitation and redox reactions, can also influence the metal circulation in the sediment pores and lower the heavy metal concentrations.

Fig. 2 demonstrates that the average heavy metal concentrations in the surface sediments from the port regions are considerably higher, measuring 211% for Mn, 152% (Fe), 205% (Co), 82% (Ni), 490% (Cu) and 463% (Zn). Those data imply that there are high concentrations of anthropogenic wastes from port activities. However, the data in Table 1 show that in the case of Mn, the concentrations in Samudera Port are lower than those in the inner bay. Thus, the biggest contributors to the increase in the average concentration of Mn in the port regions are Ferry (~399 µg/g) and Nusantara (~355 µg/g) ports; suggesting that the discharge of domestic wastes from both the ports, which are dominated by the presence of transportation and cargo ships, contain a high concentration of Mn. Comparably, Fatoki & Mathabatha (2001) reported an elevated level of Mn in the surface port sediments from East London (423 µg/g) and Port Elizabeth (358 µg/g) harbours, South Africa, which might be due to the local impact of the increasing activities of the ports. Instead, the data in Table 1 further illustrate that the concentrations of Cu (~16 µg/g) and Zn (~129 µg/g) are maximal in the samples collected from Perikanan Samudera port; this port is dominated by activities of fishing boats in the sea and fishing industry factories in the land area. Conceivably, anthropogenic sewages generated from these activities contain high concentrations of Cu and Zn. In addition, the deposition of heavy metals Cu and Zn in marine sediments is strongly dependant on redox conditions (Müller 2001). Both metals are naturally concentrated in sewage and can form very insoluble sulphides which are deposited in the coastal sediments (Förstner & Wittmann 1981). In the case of Zn, waste generated from the vessel-painting process around the port may also contribute greatly to the increased concentration of this metal in sediment. Together with Co and Pb, Zn is known as a marker of paint industries (Lin et al. 2002). Several earlier studies have emphasized that the untreated sewage from port activities had elevated the concentrations of Cu and Zn in the port sediments around the world. For instance, Kaohsiung Harbour, Taiwan contained 5~946 µg/g Cu and 52-1369 µg/g Zn (Chen et al. 2007); Elizabeth harbour, South Africa contained 9-82 µg/g Cu and 19-126 µg/g Zn (Fatoki & Mathabatha 2001); Harbour of Ceuta, Spain contained 5-865 µg/g Cu and 29-695 µg/g Zn (Guerra-García & García-Gómez 2005); Sydney Harbour, Australia contained 20-701

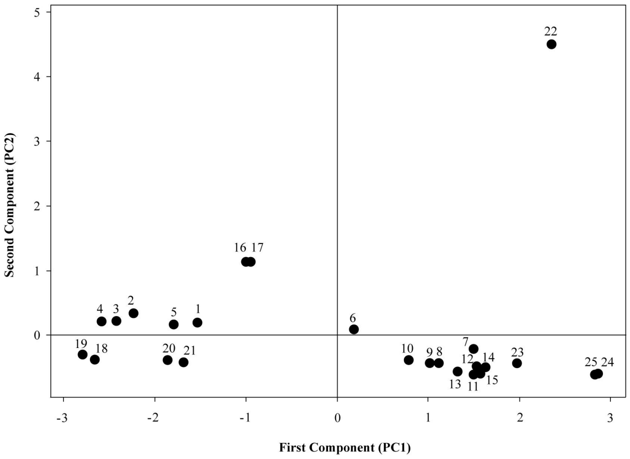

Fig. 3: Plots of PC1 and PC2 scores on the distribution of Mn, Fe, Co, Ni, Cu and Zn in 25 sampling points of Kendari Bay.

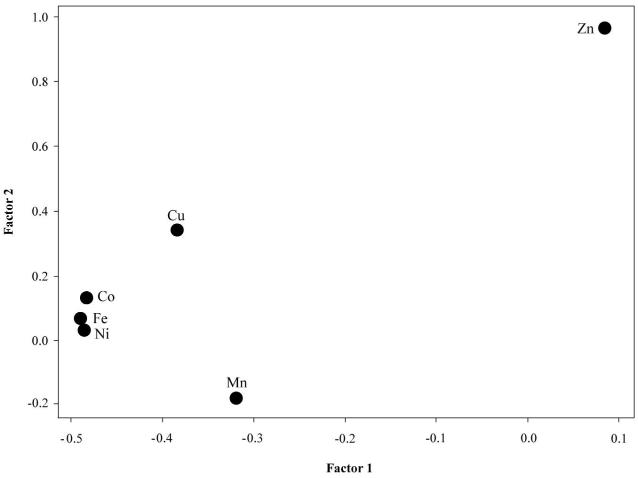

Fig. 4: The loads of variables on the two principal components.

µg/g Cu and 75-8820 µg/g Zn (McCready et al. 2006); Montevideo Harbour, Uruguay contained 58-135 µg/g Cu and 174-491 µg/g Zn (Muniz et al. 2004); Berger Harbor, Norway contained 25-1090 µg/g Cu and 46-2900 µg/g Zn (Paetzel et al. 2003).

At last, the concentrations of all heavy metals investigated in this study diminish gradually to the offshore area (Bokori Isle). The influence of the mass movement of ocean water from the Banda Sea is likely to cause dilution of heavy metals in the water system around Bokori Isle thus, reducing the concentration of heavy metals in the sediment.

We compared the data of Kendari bay with those of other locations. For instance: the concentrations of Fe found in the sediments of Gulf of Mannar (4,100-29,400 µg/g) (Jonathan et al. 2004), East China Sea (21,000 µg/g) (Fang et al. 2009) and Todos os Santos Bay (1,781-12,185 µg/g) (Pereira et al. 2015) were within the range of Kendari bay (1,100-29,800 µg/g); Jurujuba Sound (1,000-21,250 µg/g) (Neto et al. 2000) and The Croatian Adriatic coast (25-4280 µg/g) (Obhođaš & Valković 2010) had lower, but Taranto Gulf (31,566 µg/g) (Buccolieri et al. 2006) and Bay of Bengal (17,000-37,000 µg/g) (Raj & Jayaprakash 2008) exhibited higher Fe concentrations. The concentrations of other metals in Kendari bay were compared to those in other marine sediments around the world in Table 2.

Pearson correlation analysis ($p<0.05$) was performed in order to identify any relationship of heavy metals among themselves or with TOC. Of all of the heavy metals studied, only the Ni concentration shows a close positive correlation with TOC ($r = 0.62$). Because the sediment type transformation in Kendari bay is in agreement with the variation of TOC values, the distribution of Ni is associated with the fine-grained sediments of the study area. This further suggests that the distribution of other metals is strongly governed by anthropogenic inputs from the local activities of each sampling region. Pearson correlation analysis also illustrates close positive correlations between Fe and Co ($r = 0.97$), Fe and Ni ($r = 0.85$), Fe and Cu ($r = 0.57$), Fe and Zn ($r = 0.48$), while Mn reveals good relationships with those of Co ($r = 0.45$) and Ni ($r = 0.49$) only. This finding confirms that Fe compound in the surface sediments of Kendari bay is a more effective scavenger of heavy metals compared to Mn. The capability of Fe and Mn compounds, either in the form of oxides, hydroxides, carbonates and sulphides, as scavengers of metals in marine systems has been demonstrated by earlier studies (Bodur & Ergin 1994, Dang et al. 2015). Such capability is caused by their large surface area, extensive cation exchange capacity and widespread availability (Szefer et al. 1995). Furthermore, strong positive correlations are found between Co and Ni ($r = 0.83$), Co and Cu ($r = 0.61$), Co and Zn ($r = 0.51$), Ni and Cu ($r = 0.68$), Ni and Zn ($r = 0.73$) and Cu and Zn ($r = 0.89$), which suggest similar mechanisms of enrichment for these heavy metals.

Principal Components Analysis (PCA) and Hierarchical Clustering Analysis (HCA) have been performed on the data comprising 25 sampling points and 6 heavy metals (Mn, Fe, Co, Ni, Cu and Zn). Six principal components have been taken out. The first two principal components PC1 and PC2 are able to describe suitably the distribution of 25 sampling sites in Kendari bay with 76.6% of cumulative variance (Fig. 3). Fig. 3 shows that the sampling sites 1, 2, 3, 4 and 5 (Wanggu River) as well as 16 and 17 (Perikanan Samudera Port) have similar characteristics regarding the distributions of Mn, Fe, Co, Ni, Cu and Zn, indicated by negative scores on PC1 and positive scores on PC2. Furthermore, similar characteristics regarding the heavy metal distributions are displayed by the estuary (samples 7, 8, 9, and 10), inner bay

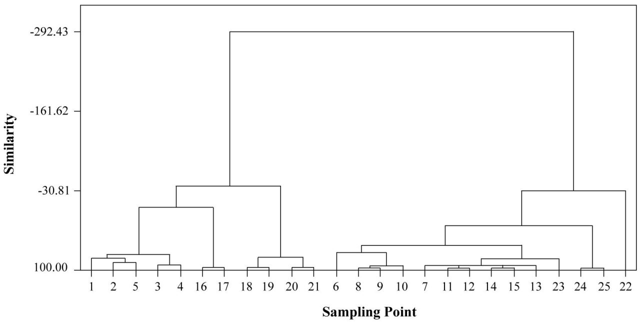

Fig. 5: Dendogram of the 25 sampling points in Kendari Bay.

(samples 11, 12, 13, 14 and 15), outer bay (sample 23) and offshore (samples 24 and 25), whereas the two sampling sites, i.e., 6 (estuary) and 22 (outer bay), have different characteristics compared to the other 23 sampling sites, as indicated by higher scores on PC1. Loading variables on the two principal components demonstrate that Fe, Co and Ni have similar distinctiveness in 25 sampling sites, specified by adjacent plot points (Fig. 4). Such distinctiveness is supported by good correlation coefficients; (r) = 0.970 ($p<0.01$) for Fe and Co correlation and 0.853 ($p<0.01$) for Fe and Ni correlation. The result of HCA by using Ward's method, applied to the Euclidean distances and illustrated by dendogram is shown in Fig. 5. There are 4 clusters formed based on the homogeneity of Mn, Fe, Co, Ni, Cu and Zn concentrations. The first cluster comprises the sampling sites in the Wanggu River (1, 2, 3, 4, 5) and Perikanan Samudera Port (16 and 17); the second cluster involves the sampling points in Ferry and Nusantara Ports (18, 19, 20 and 21); the third is the estuary (6, 7, 8, 9 and 10), inner bay (11, 12, 13, 14 and 15), outer bay (23) and offshore (24 and 25); and the fourth cluster consists of one of the sampling points in the outer bay (22). Both PCA and HCA yield a similar conclusion on the clustering of sampling sites distribution in Kendari bay surface sediments.

Geoaccumulation index: The index of geoaccumulation (I_{geo}) is used to determine the pollution level of heavy metals in sediment samples from Kendari bay. This index is a comparison of metal concentration in the study location between the recent and the pre-industrial age values. I_{geo} was first introduced by Müller (1969) with the following equation:

$$I_{geo} = \log_2 \frac{C_n}{1.5 \times B_n}$$

Where, C_n is the measured concentration of metal n and B_n is the background concentration of the metal in the average shale. Müller separated seven classes of the geoaccumulation index as follows: Class 0, I_{geo} value ≤ 0, pollution status is unpolluted; Class 1, $0<I_{geo}<1$, from unpolluted to moderately polluted; Class 2, $1<I_{geo}<2$, moderately polluted; Class 3, $2<I_{geo}<3$, from moderately to strongly polluted; Class 4, $3<I_{geo}<4$, strongly polluted; Class 5, $4<I_{geo}<5$, from strongly to extremely polluted and Class 6, $I_{geo}>5$, extremely polluted. The background concentrations of Mn, Fe, Co, Ni, Cu and Zn in the average shale are 850, 47200, 19, 68, 45 and 95 µg/g, respectively (Turekian & Wedepohl 1961). The calculation results of I_{geo} for each metal at 25 sampling sites are presented in Table 3. Based on Müller's classes of pollution level, all of the samples fall in class 0 for Mn, Fe, Co, Ni, Cu and Zn (Table 3). Hence, Kendari bay surface sediment is considered to be an unpolluted area for these heavy metals.

CONCLUSIONS

This study investigates the heavy metal pollution by Mn, Fe, Co, Ni, Cu and Zn in the surface coastal sediments around Kendari bay. The overall concentrations of Mn, Fe, Co, Ni, Cu and Zn were 34.39 to 399.59 µg/g, 1100 to 29800 µg/g, 0.24 to 7.33 µg/g, 1.14 to 15.34 µg/g, 0.6 to 15.81 µg/g and 2.58 to 129.70 µg/g dry weight, respectively, and followed the Fe > Mn > Zn > Ni > Cu > Co sequence. The Wanggu River sediments contain the highest concentrations of Fe, Co and Ni due to anthropogenic inputs, such as effluents from mining, industrial activities, agricultural runoff and household waste. The highest Mn, Zn and Cu concentrations found in port areas might be governed by local activities in the ports, including untreated anthropogenic waste containing those metals that was discharged from fishing vessels, as well as transportation and cargo ships. Of all of the heavy metals studied, only the Ni concentration shows a close positive correlation with TOC from the 25 sampling points; suggesting that the distribution of Ni is associated with the fine-grained sediments of the study area. The pollution status regarding Mn, Fe, Co, Ni, Cu and Zn in the surface coastal sediments of Kendari bay in Indonesia was calculated using the geoaccumulation index (I_{geo}). The surficial coastal sediments of Kendari bay were practically unpolluted by Mn, Fe, Co, Ni, Cu and Zn in all 25 samples.

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