Distributions and pollution assessment of heavy metals Pb, Cd and Cr in the water system of Kendari Bay, Indonesia

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Abstract. The concentrations of heavy metals Pb, Cd and Cr in the coastal waters of Kendari Bay were analyzed to assess their pollution status. Water samples from 32 sampling points were analyzed for dissolved heavy metals concentrations by using inductively coupled plasma mass spectrometry (ICP-MS). The RSD(%) of each metal was accounted to analyze the diversity of the heavy metals among 32 sampling points. The results demonstrate that the dissolved heavy metal Pb had the highest concentrations (0.009 to 0.549 μg/L, average = 0.210 μg/L) followed by Cr (0.085 to 0.386 μg/L, average = 0.149 μg/L), and Cd (0.001 to 0.015 μg/L, average = 0.008 μg/L). Based on the the RSD values (Pb = 87.8%, Cd = 45.2% and Cr = 41.3%), it is suggested that the antropogenic activities controls the high diversity of concentrations for heavy metal Pb relative to those of Cd and Cr. Comparing the data with the mean oceanic concentrations, only the concentrations of Pb exceed the mean oceanic level (210 folds). Therefore, the water system of Kendari Bay is severely polluted with heavy metal Pb. More management and treatment should be introduced to protect the marine environment in the study area, especially from Pb pollution.

1. Introduction
The increase of human populations and industrial activities have considerably contributed to the weakening in water quality, including accumulation of heavy metals in the coastal waters [1-3]. Heavy metals are among the most common environmental pollution and their occurrence in water system indicate the presence of natural or anthropogenic sources, such as geologic weathering, mining practices, industrial activities, urban development, as well as deposition from the atmosphere [4-7]. The behaviors 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 bio-magnification in marine systems [8-10].

Kendari Bay is a fringing bay located in Kendari City, in the Province of South East Sulawesi, Indonesia. The bay has attracted increased human activity over the years, and industries such as tourism, transportation, fishing and shipping thrive along the coastal area in the city. The Wanggu River system flow, which is connected directly to the western part of the bay, may become a source for the input of heavy metals to the bay. To date, research into the heavy metal distribution in this
location has been scarce. Accordingly, it is quite important to understand the distribution and pollution status of heavy metals in the water environments of Kendari Bay in order to manage the quality of water in estuarine and coastal areas. The aim of the current study is to investigate the distribution of the heavy metals Pb, Cd and Cr in coastal waters of Kendari Bay in order to consider their sources and pollution status.

2. Materials and methods

2.1. Study location
Kendari Bay is a fringing bay located at 3°58’ S and 122°34’ E and has an area of 10.84 km² (figure 1). The Wanggu River, the largest river in Kendari, has a mouth at the western part of the bay. There are three ports located at the eastern part of the bay, i.e. Ferry, Perikanan Samudera and Nusantara Ports, which are directly connected to the Sunda Sea. The ports are mainly used for commercial purposes such as ferry service (Ferry Port) and fish landing center (Perikanan Samudera Port). Loading and unloading of industrial containers from big cargo ships also undergoes at Nusantara Port. Coral reefs are found to survive at the Bokori Isle, which is located at the eastern part of the bay. Bokori Isle is used as a tourist destination which is managed by local government.

Figure 1. Map showing Kendari Bay, South East Sulawesi, Indonesia. Filled circles indicate the sampling points

2.2. Sampling
All polyethylene vessels used to collect and store water samples were pre-washed by 10% nitric acid, and rinsed with Milli-Q water before they were oven-dried at 40°C. Water samples were collected during October 2014 from 32 sampling points ranging from the lower reaches of the Wanggu River to the offshore region of Kendari Bay (figure 1). The points are clustered into 5 sampling regions, including Wanggu River (1, 2, 3, 4, 5, 6, 7, 8, 9 and 10), estuary (11, 12, 13, 14, 15, 23 and 24), inner bay (16, 17, 18, 19, 20, 21 and 22), ports (25, 26, 27, 28, 29 and 30) and offshore (31 and 32). All samples were filtered through a Millipore HA filter (0.45 µm pore size), added with concentrated nitric acid (Kanto Chemical Co., Inc., Tokyo, Japan) to meet the final solution of 1% nitric acid, and then preserved at 4°C until analysis.

2.3. Analysis
Samples were measured directly without pre-concentration by inductively coupled plasma mass spectrometry (ICP-MS) (Thermo Scientific™ XSERIES 2 ICP-MS, Germany). Each measurement of heavy metals was run in triplicate and the concentrations of metals were quantified by calibration methods using SPEX XSTC-331 as a multi-elemental standard solution. The detection limits for Pb,
Cd and Cr were 0.001, 0.004 and 0.019 µg/L, respectively. The accuracy of the measurement was assessed using NASS-5, the seawater reference material for trace metals from National Research Council (NRC), and yielded 97, 105 and 95% recoveries for Pb, Cd and Cr, respectively (table 1). 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).

| Metal | Certified | Measured ±SD (n = 10) | Recovery (%) |
|-------|-----------|------------------------|--------------|
| Pb (ppb) | 0.008 | 0.0078±0.002 | 97 |
| Cd (ppb) | 0.023 | 0.0242±0.008 | 105 |
| Cr (ppb) | 0.110 | 0.1044±0.011 | 95 |

3. Results and discussion

3.1. Trends in heavy metal concentrations

The distributions of heavy metals in the coastal waters of Kendari Bay in each sampling point are tabulated in Table 2. The concentrations of dissolved heavy metals Pb, Cd and Cr are 0.009-0.549 µg/L (average = 0.210 µg/L), 0.001-0.015 µg/L (average = 0.008 µg/L) and 0.085-0.386 µg/L (average = 0.149 µg/L), respectively. The relative standard deviation (RSD, %) was used to analyze the diversity of heavy metals among 32 sampling points. The RSD of heavy metal Pb (~88%) was higher than those of Cd (~45%) and Cr (~41%); suggesting that the distribution of Pb was more controlled by the anthropogenic input at each sampling point and yielded higher diversity of Pb concentrations than other two metals.

The fluctuations of mean concentrations of heavy metals based on the sampling region are showed in figure 2. The trends of Pb concentrations associated with sampling region following the order: Wanggu River > inner bay > estuary > ports = offshore. For the case of Cd, the highest concentrations were found in the offshore regions, while Wanggu River, estuary, inner bay and ports regions has similar concentrations. Cr following the order: Offshore > Wanggu River > estuary > inner bay > ports. Taking into consideration that the Wanggu River, the biggest river in Kendari City, as the main source of input of inorganic elements (such as metals) to Kendari Bay [1], it is surprisingly to note that there are significant elevations of heavy metals Cd and Cr in the offshore region beyond to the levels in Wanggu River (figure 2).

![Figure 2. Mean concentrations of heavy metals in each sampling region](image)

As the main entry of inorganic elements, the high accumulation of heavy metals (mainly Pb) in the samples derived from Wanggu River may come from anthropogenic inputs such as untreated sewage predominantly from mining activities, besides agricultural runoff and household waste. It has to be...
noted that there are recently 150 ore mining companies located in the districts of North Konawe, Konawe and South Konawe which they are in the passageway by the Wanggu River [11]. Accordingly, the waste generated from mining activities can be entered into Wanggu River directly or indirectly, and increase the accumulation of heavy metals in the water system of the lower reaches of the river. Additionally, the highest Pb concentration found in the Wanggu River may originated from the atmospheric loading (such as combustion and road-side dust) which is transported to the river system during runoff and rainfall events [12-14].

**Table 2.** Heavy metals Pb, Cd and Cr concentrations in the coastal waters of Kendari Bay

| Sampling region               | Sampling point | Concentration (μg/L) | Pb  | Cd  | Cr  |
|-------------------------------|----------------|----------------------|-----|-----|-----|
| Lower reaches of Wanggu River | 1              | 0.501                | 0.007 | 0.157 |
|                               | 2              | 0.413                | 0.005 | 0.133 |
|                               | 3              | 0.511                | 0.004 | 0.187 |
|                               | 4              | 0.433                | 0.008 | 0.135 |
|                               | 5              | 0.473                | 0.007 | 0.386 |
|                               | 6              | 0.549                | 0.010 | 0.190 |
|                               | 7              | 0.357                | 0.008 | 0.158 |
|                               | 8              | 0.322                | 0.008 | 0.143 |
|                               | 9              | 0.48                 | 0.003 | 0.135 |
|                               | 10             | 0.522                | 0.007 | 0.196 |
|                               | Average        | 0.456                | 0.007 | 0.182 |
| Estuary                       | 11             | 0.215                | 0.004 | 0.119 |
|                               | 12             | 0.104                | 0.012 | 0.122 |
|                               | 13             | 0.021                | 0.001 | 0.119 |
|                               | 14             | 0.054                | 0.012 | 0.086 |
|                               | 15             | 0.218                | 0.008 | 0.261 |
|                               | 23             | 0.087                | 0.007 | 0.115 |
|                               | 24             | 0.117                | 0.012 | 0.116 |
|                               | Average        | 0.117                | 0.008 | 0.134 |
| Inner bay                     | 16             | 0.186                | 0.009 | 0.132 |
|                               | 17             | 0.275                | 0.006 | 0.160 |
|                               | 18             | 0.200                | 0.009 | 0.155 |
|                               | 19             | 0.025                | 0.012 | 0.103 |
|                               | 20             | 0.054                | 0.004 | 0.123 |
|                               | 21             | 0.113                | 0.007 | 0.107 |
|                               | 22             | 0.052                | 0.012 | 0.094 |
|                               | Average        | 0.129                | 0.008 | 0.125 |
| Ports                         | 25             | 0.069                | 0.003 | 0.136 |
|                               | 26             | 0.060                | 0.005 | 0.095 |
|                               | 27             | 0.023                | 0.008 | 0.122 |
|                               | 28             | 0.061                | 0.006 | 0.104 |
|                               | 29             | 0.009                | 0.005 | 0.085 |
|                               | 30             | 0.095                | 0.014 | 0.122 |
|                               | Average        | 0.053                | 0.007 | 0.111 |
| Offshore                      | 31             | 0.042                | 0.014 | 0.225 |
|                               | 32             | 0.068                | 0.015 | 0.244 |
|                               | Average        | 0.055                | 0.015 | 0.235 |
| Total Average                 | 0.210           | 0.008                | 0.149 |
| Total RSD (%)                 | 87.75           | 45.24                | 41.28 |
Figure 2 further shows that, except for Cd, there is a decrease in heavy metals concentrations significantly by 74.34% (for heavy metal Pb) and 26.37% (for Cr) in the estuarine areas in comparison to the lower reaches of the Wanggu River. Estuary region of Kendari Bay is an area populated mostly by mangroves. A decrease in the concentrations of heavy metals in the estuarine water likely to be caused by the so-called phytoremediation, a process of absorption of dissolved metals from the surrounding environment to the mangrove tissues. The ability of mangroves to perform the phytoremediation process has been widely investigated by earlier studies (e.g. [15-17]). [18] has emphasized specifically the capability of mangrove trees in the Brazilian coastal areas to uptake metals ion like Pb, Cd and Cr in their bodies. Nevertheless, the phytoremediation ability by mangrove is different between one species to another, besides it is also controlled by the concentration of heavy metal exists in the surrounding environment [19]. The very low concentration of Cd distributed in the seawater of the estuary region (0.008 mg/L in average, table 2) is likely to cause mangrove species that grow in that region cannot perform phytoremediation optimally.

Entering the inner bay, the concentrations of heavy metal Pb are increased by ~11% and the Cr concentrations decreased ~7%, while the Cd remains constant relative to the estuary levels. The middle area of Kendari Bay is highly correlated with the household wastes that come from the surrounding areas. The distribution of heavy metals in the inner bay may be affected by the tide and physicochemical recycling generated by the water mass movement in this area, increasing or decreasing the heavy metals concentrations in the aquatic system. Moreover, figure 2 shows that there are declines in heavy metals Pb and Cr concentrations from the inner bay to the ports areas of Kendari Bay. The Pb concentrations are reduced by 59%, while the Cr is reduced by 11%. These data indicate that several anthropogenic activities in the ports, such as transportation, shipping and fishery, do not enhance the accumulation of heavy metal concentrations in the water system of the region. In general, therefore, it seems that the heavy metals from water system were removed to the ports sediments. The heavy metals (including Pb, Cd and Cr) might be active in the reduction-oxidation processes whereby they dominated the soluble fraction under oxygenated conditions and precipitated straightaway when post-oxic conditions were encountered [20].
increased by 59%, while the Cr is increased by 11% relative to the Wanggu River samples. It is well thought-out that the offshore region which is closed to Bokori Isle is relatively not affected by the heavy metal drive from the entry point at Wanggu River as the isle is located far away from the lower reaches of the river. In addition, the open water activity and the influence of seawater current movements from the Banda Sea might wash away and diluted the heavy metals present in offshore region. An implication of this is the possibility that the anthropogenic activities around Bokori Isle, such as tourism, transportation and fishing practices, have substantial amounts of wastes containing heavy metals Cd and Cr discharged into coastal waters around Bokori Isle and led to the high accumulation of those metals in the offshores.

Principal Components Analysis (PCA) and Hierarchical Clustering Analysis (HCA) have been performed on the data comprising 32 sampling points and 3 heavy metals (Pb, Cd and Cr). Three principal components have been taken out. The first two principal components PC1 and PC2 are able to describe suitably the distribution of 32 sampling points in Kendari Bay with 85.6% of cumulative variance (figure 3). Figure 3 shows that the sampling points 1, 2, 3, 4, 6, 7, 8, 9 and 10 (Wanggu River), as well as 16, 17 and 18 (Inner bay) have similar characteristics on the distributions of Pb, Cd and Cr, indicated by the location of PC1 and PC2 adjacent to each other. Four sampling points, i.e., 5 (Wanggu River), 15 (estuary), 31 and 32 (offshores), have different characteristics on Pb, Cd and Cr distributions compared to the other 32 sampling sites, as indicated by higher scores on PC1. Similar characteristics regarding to the heavy metals distributions are also displayed among estuary (samples 12, 14 and 24), inner bay (samples 19 and 22), and port (sample 30), which are differentiated by negative scores on the PC1 and positive scores on PC2. Furthermore, the same characteristics on the heavy metals trends are found in the samples 11, 13 and 23 (estuary), 20 and 21 (inner bay), 25, 26, 27, 28 and 29 (ports), where both PC1 and PC2 scores are negative.

Loading variables on the two principal components demonstrate that Pb and Cr have similar characteristics in 32 sampling points, specified by adjacent plots (figure 4). Such similarity is supported by a linear correlation coefficient (r) 0.454 (p<0.01). The result of HCA by using Ward’s method and applied to the Euclidean distances indicates 4 clusters formed based on the homogeneity of Pb, Cd and Cr concentrations. The first cluster comprises the sampling points 1, 2, 3, 4, 6, 7, 8, 9, 10, 16, 17 and 18; the second cluster involves the sampling points 5, 15, 31 and 32; the third is 12, 14, 19, 22, 24 and 30; and the fourth cluster consists of the sampling points 11, 13, 20, 21, 23, 25, 26, 27, 28 and 29. Please note that, based on HCA, samples 31 and 32 are located on the similar cluster;
supporting the idea that the anthropogenic activities play an important role in the heavy metals distributions in this region, particularly the heavy metals Cd and Cr, as is mentioned earlier. Both PCA and HCA yield a similar conclusion on the clustering of sampling points distribution in Kendari Bay coastal waters.

3.2. Heavy metals pollution
In order to infer the pollution status, the dissolved heavy metals concentrations of the surface waters in the Kendari Bay were compared with the Seawater Quality Standard of Indonesia [21] as well as the normal composition of seawater [22], as shown in Table 3.

| Reference | Point                          | Concentration (µg/L) |
|-----------|--------------------------------|----------------------|
| This study | Kendari Bay                    | 0.210* 0.008* 0.149* |
| [21]      | Seawater quality standard of Indonesia | ≤5  ≤2  ≤2   |
| [22]      | Mean oceanic concentration     | 0.001  0.07  0.33 |

* = average concentration from 32 sampling points (Table 2)

Table 3 shows that the average concentrations of heavy metals Pb, Cd and Cr found in Kendari Bay coastal waters did not exceed the seawater quality standard of Indonesia [21]. However, comparing the data with the mean oceanic concentrations [22], the concentration of heavy metal Pb was considerably higher than its mean oceanic level by 210 folds; implying a serious pollution. This research has thrown up in need of further management works in the study area in order to protect marine environment from the pollution of heavy metals, especially Pb.

4. Conclusions
This study investigates the distribution of heavy metals Pb, Cd and Cr in the coastal waters around Kendari Bay. The overall concentrations of Pb, Cd and Cr were 0.009 to 0.549 µg/L (average = 0.210 µg/L), 0.001 to 0.015 µg/L (average = 0.008 µg/L) and 0.085 to 0.386 µg/L (average = 0.149 µg/L), respectively, and followed the Pb > Cr > Cd sequence. Wanggu River, the biggest river in the city, is the main entry of heavy metals (especially Pb) to the water system in Kendari Bay, in addition to the agricultural runoff, household waste and atmospheric loading. Based on the RSD values, this study shown that the anthropogenic activities control the high diversity of concentrations for heavy metal Pb relative to those of Cd and Cr. One of the more significant results to emerge from this study is that the concentration of heavy metal Pb in the water system of Kendari Bay is considerably higher by 210 folds than the mean oceanic level. Accordingly, further management works is required to protect marine environment in Kendari Bay from the Pb pollution.

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