



Contents lists available at ScienceDirect

## Marine Pollution Bulletin

journal homepage: [www.elsevier.com/locate/marpolbul](http://www.elsevier.com/locate/marpolbul)

## Baseline

## The distribution of heavy metals including Pb, Cd and Cr in Kendari Bay surficial sediments

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## ARTICLE INFO

## Keywords:

Heavy metals  
Geoaccumulation index  
Kendari Bay  
Pollution status

## ABSTRACT

The surficial coastal sediments in Kendari Bay are sampled in the field to determine the concentration and pollution level of three heavy metals (Pb, Cd and Cr). Twenty-five sampling points ranging from the inner (Wanggu River) to the outer area of the bay have been chosen. The physicochemical properties, such as temperature, pH, salinity and TDS of the overlying water, as well as the sediment type and TOC of the surficial sediments, are also measured. The total concentrations of the Pb, Cd and Cr in the sediment samples are quantified using inductively-coupled plasma mass spectrometry (ICP-MS). The concentrations of the heavy metals (Pb, Cd and Cr) ranged from 0.84 to 17.02 µg/g, 0.02 to 0.17 µg/g and 1.92 to 40.11 µg/g (dry weight), respectively, following the Cr > Pb > Cd sequence. To assess the degree of contamination, a geoaccumulation index ( $I_{geo}$ ) is measured. Kendari Bay is not a contaminated area regarding Pb, Cd and Cr.

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Estuarine and coastal environments are dynamic and complex aquatic systems due to environmental factors, such as the physical, chemical, and biological interactions between freshwater and saltwater (Wu et al., 2011). The existence of pollutants (such as heavy metals) within aquatic systems has become a pressing concern for environmentalists in recent years due to the toxicity of these elements. After entering the hydrosphere, heavy metal could be carried from its source, possibly affecting the life of aquatic organisms and human health. Both estuaries and coastal areas are subject to the varying influences of anthropogenic and atmospheric inputs, coastal and seafloor erosion, and biological activities that may affect the transport and fate of heavy metals. However, the physicochemical transport and biogeochemical interactions within these systems may play critical roles in controlling the circulation of heavy metals within these systems (Ip et al., 2007).

The concentrations of heavy metals may be higher in the coastal sediments and suspended particulate matter than that in the overlying seawater due to the strong adsorption of these compounds to sediment. Consequently, coastal sediments act as a large heavy metal sink in oceanic systems (Olsen et al., 1982). The existence of heavy metals in coastal sediments can pose

serious environmental problems associated with water quality and bioaccumulation in marine organisms. Therefore, coastal sediments are geochemically important components of the marine environment that provide useful information for environmental and geochemical research concerning marine pollution.

Since the beginning of the industrial revolution and the subsequent increase in industrial development, very large amounts of toxic pollutants have been discharged into coastal and estuarial environments, contaminating marine sediments with heavy metals (Farmer, 1991; Liu et al., 2003; Perkins et al., 1973). Earlier studies have revealed a significant global elevation in heavy metal polluted oceanic sediments in recent decades. The heavy metals contaminating coastal environments are produced by mining practices, industrial activities, urban development and other human activities near rivers and estuaries, as well as deposition from the atmosphere (Balls et al., 1997; Bird et al., 2005; Morton and Blackmore, 2001; Nriagu, 1996; Taylor and McLennan, 1995; Zingde et al., 1988).

Kendari Bay is an outlying bay located in Kendari City in the Province of South East Sulawesi in Indonesia. The bay has become a hub for tourism, transportation, fishing and shipping along the coastal area in the city. The Wanggu River system and the three ports located inside the bay (Ferry, Perikanan Samudera and Nusantara Ports) may provide nutrients and influence the chemical characteristics of the metals in the water and sediment of the

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bay. To date, research regarding the metal distribution of sediments in this location remains scarce. Accordingly, understanding the geochemical distribution and pollution status of heavy metals in sediments of Kendari Bay is important for managing the water quality in the estuarine and coastal areas. The current study assesses the Pb, Cd and Cr concentrations in the surficial coastal sediments of Kendari Bay and investigates the trends in these values compared to other coastal areas worldwide. The influence of the sediment properties (grain size and total organic matter) on the metal concentrations was also investigated. A geoaccumulation index ( $I_{geo}$ ) was estimated to quantify the pollution status of the Kendari Bay sediments.

Twenty-five sampling points ranging from the Wanggu River downstream area to the offshore area of Kendari Bay is shown in Fig. 1. The points are grouped into 6 sampling areas: the Wanggu River (A1, A2, B1, B2 and B3), the estuary (A3, A4, B4, B5 and B6), the inner bay (A5, A6, A7, B7 and B8), the ports (A8, A9, A10, A11, A12 and A13), the outer bay (B9 and B10) and the offshore area (A14 and A15). The surficial sediments of A1 to A15 sampling points were collected on April 1, 2013 while those of B1 to B10 were sampled three days later with an Ekman grab sampler. It is considered that no significant modifications in sediment chemistry as there was no abrupt changes on the weather during two periods of sampling. To avoid contamination from the metal sides of the grab, the sediments were subsampled from the center of the collected material using a plastic spatula. The sediment samples were inserted directly into plastic bags to minimize any atmospheric contamination and were stored inside an icebox. The samples were stored at  $-20^{\circ}\text{C}$  in the laboratory before analysis. During sampling, the physical and chemical properties of the overlying water (i.e., temperature, pH, salinity and TDS) were directly measured with a portable pH-salinity-TDS meter (Jenway 430, UK).

In the laboratory, the samples were dried at room temperature until they reached a constant weight; subsequently, they were ground until homogeneous in a mortar and passed through a 100- $\mu\text{m}$  sieve. A portion of each sediment sample (approximately 0.06 g) was placed in a Teflon beaker with 1.2 ml of conc.  $\text{HNO}_3$  (Kanto Chemical Co., Inc., Tokyo, Japan) and 0.15 ml (~5 drops) of HF (Kanto Chemical Co., Inc., Tokyo, Japan), heated on a hot plate to  $80^{\circ}\text{C}$  and left for overnight for digestion. The solution was diluted to 30 ml with Milli Q-water before 3 ml aliquots of this solution were diluted with Milli Q-water to 6 ml, generating the samples for the inductively-coupled plasma mass spectrometry (Thermo Scientific™ XSERIES 2 ICP-MS, Germany) measurements of the heavy metals Pb, Cd and Cr. Each sample measurement

was performed in triplicate. SPEX XSTC-331 was used as multi-elemental standard solution during the analysis. The concentrations of the metals are reported in  $\mu\text{g/g}$  dry weight. A blank was prepared using amounts of acids similar to those in the digestion process. The accuracy of the method was confirmed by analyzing marine sediment reference material (NMIJ CRM 7302-a), revealing good agreement between the certified and the measured values (Table 1). The detection limit of the method was 4.1, 0.1 and  $23.5\text{ ng g}^{-1}$  (dry weight) for Pb, Cd and Cr, respectively. Furthermore, other portions of the sediment were subjected to TOC analysis with a Carlo Erba NA-1500 Analyzer and grain size analysis via sieving for the coarse fraction; a particle size analyzer (a SediGraph III 5120) was used for the fine fraction. Grain sizes from 2000 to  $62.5\text{ }\mu\text{m}$  are classified as sand,  $62.5$  to  $3.9\text{ }\mu\text{m}$  are silt and those samples below  $3.9\text{ }\mu\text{m}$  are clay (Wu et al., 2011).

Principal component analysis (PCA) and hierarchical clustering analysis (HCA) were performed for the concentrations of heavy metals by using the computer program MINITAB 17.1.0.0 (Minitab Inc., State College, Pennsylvania, USA) in order to interpret the correlation existing among the heavy metal distributions within the sampling points.

Table 2 lists the type and TOC of the surficial sediments, as well as the physicochemical properties of the overlying water during sampling (temperature, pH, salinity, TDS). The sediment types gradually transform from silt (Wanggu River), sandy silt (estuary, inner bay, ports), silty sand (ports, outer bay) and sand (offshore). The similarity between the sediment types found in estuary, inner bay and ports (sandy silt) as well as ports and outer bay (silty sand) indicates a long-standing and stable depositional marine environment in Kendari Bay. Moreover, the open water activity and the influence of seawater current movements in the Banda Sea might wash away the finer particles; therefore, the offshore area was dominated by sand. This transformation between sediment types agrees with the variations in the TOC values (TOCs of silt > sandy silt > silty sand > sand). The TOC values range from 1.23 (offshore) to 2.66% (Wanggu River) and average 2.14%. Therefore, the high organic carbon content in the Wanggu River is exported through the estuary toward the inner bay. Previous studies have revealed the correlation between the TOC and particle size of marine sediment. High TOC values are normally associated with finer sediment, while low TOC occurs with coarser sediment (Balls et al., 1997; Caccia et al., 2003; Cho et al., 1999; Wu et al., 2011). Accordingly, TOC plays an important role in geochemical behavior and in determining the fate of trace metal deposited in marine sediment (Fang and Hong, 1999; Fang et al., 2009; Lin et al., 2002). This value

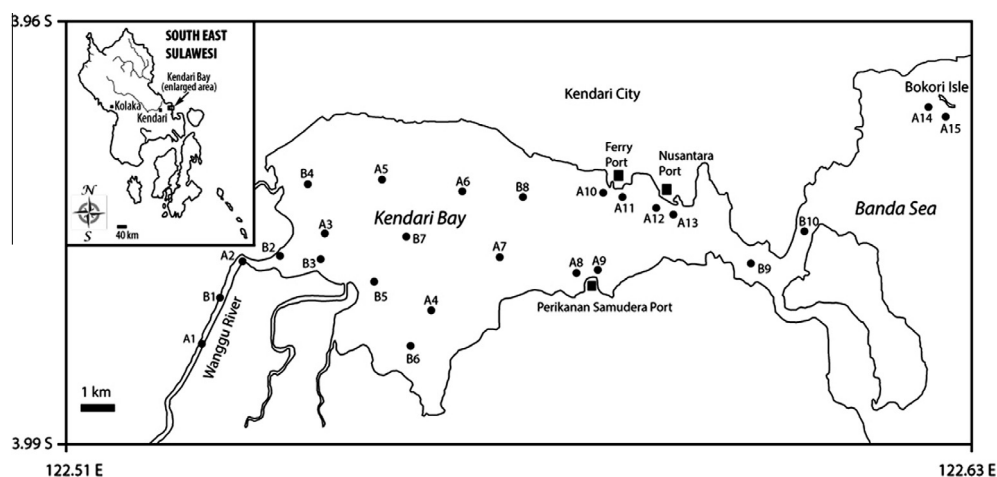


Fig. 1. Sampling points in Kendari Bay.

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