Spatial Distribution of Dissolved Heavy Metals (Hg, Cd, Cu, Pb, Zn) on the Surface Waters of Pare Bay, South Sulawesi

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Abstract

Pare bay is one of the areas of significance which is utilized for port services, stevedoring, oil distribution, regional industrial development, aquaculture, cultivation and settlement systems. Pare Bay potentially has a good prospect for a gigantic development. Whilst, a very dangerous threat is pollution, especially heavy metal pollution and water quality degradation. This study aims to determine the current condition of heavy metal concentrations and its distribution on surface waters of Pare Bay. Heavy metals were analyzed using AAS (Atomic Absorption Spectrophotometry) in which it has a minimum detection limit reached 0.001 ppm so that the heavy metal concentration can be well-determined. Hg concentration is higher in the surface ranged 0.01-0.1 mg.l^{-1}. Cd concentration ranged from 0.018-0.083 mg.l^{-1}. Cu concentration ranged from 0.043-0.078 mg.l^{-1}. Pb concentration ranged from 0.111-2.692 mg.l^{-1}. Zn concentration ranged from 0.004 - 0.112 mg.l^{-1}. Heavy metals content in Pare Bay exceeds the standard quality established by Ministry of Environment. It potentially harms the marine life which indirectly reduces the function value of Pare Bay as a center of maritime in the South Sulawesi. Water quality condition play a role in inducing the toxicity level of heavy metals in the Pare Bay. So that this area need to be monitored the water quality sustainably.

Keywords: *AAS, water quality, pollution, Pare Bay*

Introduction

The municipality of Pare Pare is a region located in South Sulawesi, which is a key region of South Sulawesi Province. Pare Pare is the center of food sector development which serves as the center of port services, stevedoring, oil distribution, industrial development areas, aquaculture (seaweed), as well as settlement systems (Wahab and Mutmainnah, 2005). Several issues appeared due to the development present time such as water pollution, water quality degradation, and heavy metal pollution.

Pare Bay is potentially contaminated by heavy metal. Based on the data, content of heavy metal residues in water, soil and fisheries commodities in South Sulawesi Province are very alarming such as Pb (0.4751 mg.l^{-1}), Hg (0.0054 mg.l^{-1}) and Cd (0.0391 mg.l^{-1}) (Departemen Perikanan dan Kelautan, 2008). Pare Bay has prospects for a gigantic development, as a result, it can pollute the surroundings. Heavy metal pollution is one of the issues occurred in the Pare Bay (Usman *et al.*, 2013).

Water quality degradation occurred in Pare Bay is caused by the presence of contaminants, both in the form of organic and inorganic compounds. One of the dangerous inorganic compounds is heavy metal. Some heavy metals are widely used in a variety of everyday purposes. Therefore, routinely produced in industrial scale. The use of these heavy metals probably will pollute the environment, that mainly is mercury (Hg), Lead (Pb), Copper (Cu), Cadmium (Cd) and zinc (Zn) (Fitriani *et al.*, 2014).

Heavy metals pollution can be induced by oil spills that sources from operation, repairation and maintenance of ships, and bunkers, moreover it is worsened by loading and unloading of oil, offshore building and tanker accidents as well (Supardi *et al.*, 2014). Naturally, heavy metal enters the aquatic environment because of rocks abrasion (erosion), minerals and metal dust (the particulate matter contained in the layer of the air which is brought down by the rain accumulated in the water) (Palar, 1994). Heavy metal concentration enhancement could adversely affect the quality of the catched-fish and aquaculture in the Pare Bay. The process takes place continuously. The amount of metal consumed

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will also increase. Eventually, it will be accumulated in the human body (Darmono, 1995). Based on the description above, this study was conducted to determine the current condition and distribution of heavy metals in the surface water of Pare Bay and its impact on Pare Bay as the maritime center of South Sulawesi.

Materials and Methods

The research location situated inner and outer Pare Bay, Makassar Strait (Figure 1.) which consist of 28 observation stations. The water sampled was then analyzed in the Laboratory of Soil Installation Assessment Institute of Food Technology (BPTP) Maros, South Sulawesi.

Water sampling was done during the displacement of high to low tidal condition (Figure 2.) based on tide forecasting using NAOtide software for coordinate longitude 119.5976 and latitude -4.0234. Each sample was taken at the same tidal condition, so the heavy metals and water quality distribution could be well compared. Data were collected on the 15th September at 09:00-14:00 pm. Water samples were taken using *Van Dorn Water Sampler* which has a capacity of 2 liters. The samples only represent the surface water. Samples were stored in polyethylene bottles. It was then cooled in a cool box for further laboratory analysis. In the laboratory, sample for heavy metals analysis was filtered using filter paper Nucleopore (pore size 0.45 μm) which had soaked with 6N HCL for a week and rinsed with distilled water. It was then added HNO_3 (pH<2) (Maslukah, 2007). The filtered paper was then dried in the oven. It was used to calculate the heavy metal content in the filtered water. Calculation of heavy metal used AAS (Atomic Absorption Spectrophotometry) which has a minimum detection limit 0.001 ppm (Maslukah, 2007). Water quality parameters measured *in situ* at the same sampling point are temperature, pH, and salinity.

The sample was weighed as much as 2 grams which was then heated in a furnace with temperature of 550°C. After that, it was cooled in a desiccator then added 20ml and 2ml HNO_3 $HClO_4$. The solution heated on a hot plate was then filtered. Filtrate samples obtained incorporated into 50 mL volumetric flask. To match the volume, we used distilled water. Heavy metals (Pb, Cd, Cu, Zn and Hg) were analyzed using AAS at certain wavelengths. Linear regression equation of absorbance of the reference solution is made. The solution absorbance resulted were plotted into the curve of a standard solution. The concentration obtained in the form of $mg.l^{-1}$ (Wahab and Mutmainnah, 2005).

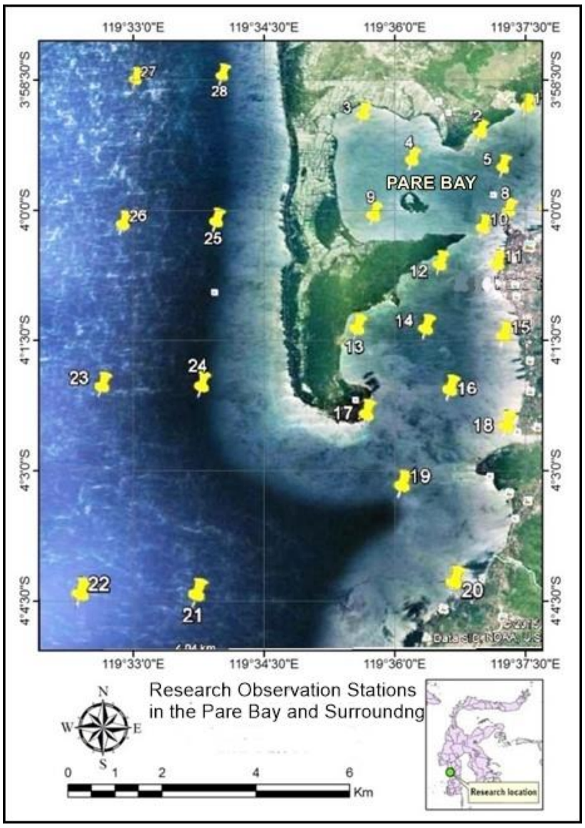

Figure 1. Distribution of sampling points (Google Earth, 2015)

Spatial analysis using geographic information system (GIS) has been widely used for various studies of aquatic resources. GIS analysis can provide full display in an area. The renewal of the analysis can be easily done if the latest data are available (Johnston, 1998). But the implementation must be proportional representing the study area. So that the analysis can be better and more visible the degradation resulted. GIS application showing the condition of the aquatic environment has been widely published (Radiarta, 2013). Study of water environmental condition spatially is often used to analyze the distribution of the concentration of chemical and physical parameters in the water.

Spatial analysis technique *inverse distance weighted* (IDW) was employed (Johnson and McChow, 2001), performed to analyze the distribution of heavy metal concentrations in Pare Bay during low tidal condition, so it can be determined how the distribution and deposition processes of heavy metals within the bay and surrounding. IDW Set-up is shown in Table 1.

Water quality data were measured *in situ* using *TOA DKK water quality Checker.* The parameter measured are pH, Temperature and salinity. The result was analyzed statistically (Table 2).

Results and Discussion

Mercury (Hg) concentration ranged from 0.01-0.1 mg.L-1 in the surface layer cannot be identified in the several stations, such as at station 7-9 and 16-20 as well as station 22 (Figure 3.). While, in the 5 m depth, the minimum concentration of Hg reached 0.02 mg.l^{-1} and the maximum reached 0.09 mg.l^{-1}. The undetectable concentrations observed at station 7-8 and 15-17 as well as station 19 (Figure 4.). The amount of mercury is quite high exceeding the quality standard established by Ministry of Environment (2014) that is equal to 0.03 mg.l^{-1} (port environment), 0.002 mg.l^{-1} (nautical tourism) and 0,001 mg.l^{-1} (marine tourism). The high concentration of Hg was observed in the northern Pare Bay.

Table 1. IDW set up for interpolation spatial analysis

Parameter	Implemented in the interpolation
Projectionted coordinate system	UTM Zone 50 Southern Hemisphere World Geographic System (WGS) 1984
Geoprocessing-Environment Setting	Processing Extend : Top = 9562412,394119 Bottom = 9554782,274561 Left = 786718,391947 Right = 795527,277366
ArcToolbox - Spatial Analyst Tool	IDW Set up : Output Cell Zise = 30,5204782322347 Number Of Points = 12 Search Radius = Variable

Table 2. Desciptive statistic of Water Quality parameters

Variable	Mean	St Dev	Max	Min	Median
pH	7,8	0,10	7,93	7,47	7,82
Temperature (°C)	27,98	0,36	28,6	27,2	28,1
Salinity (‰)	31,54	2,18	32,9	31,73	31,85

(Source: Data processing, 2015)

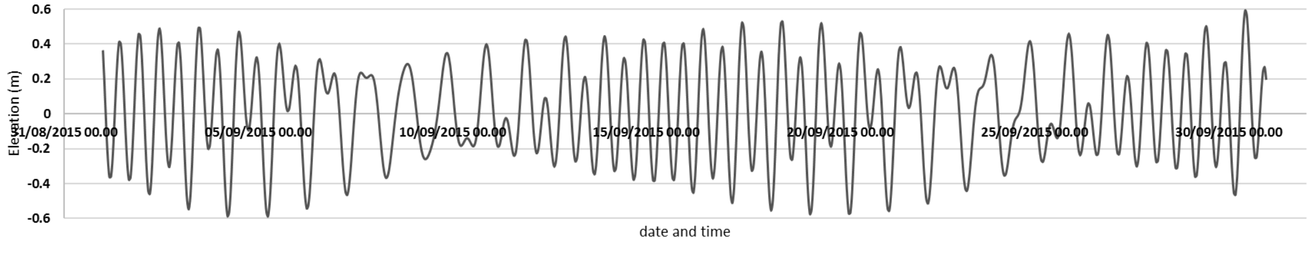

Figure 2. Tide Forecasting by Naotide

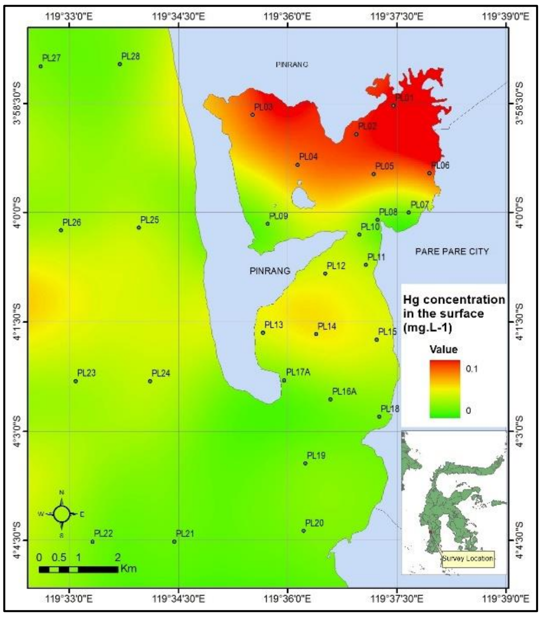

Figure 3. Hg distribution in the surface

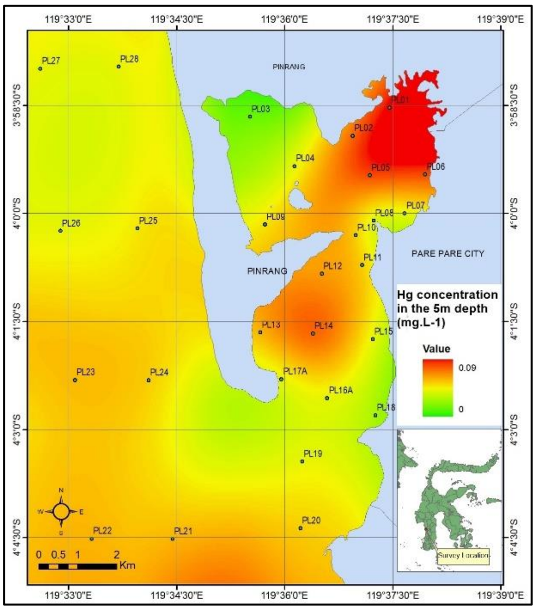

Figure 4. Hg distribution in the 5m depth

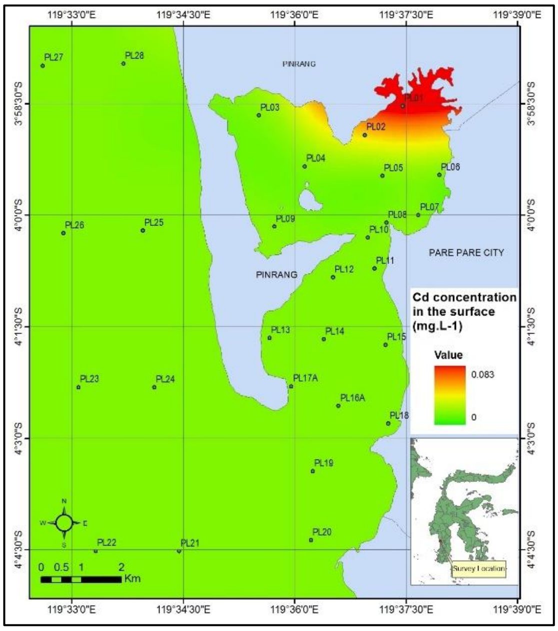

Figure 5. Cd distribution in the surface

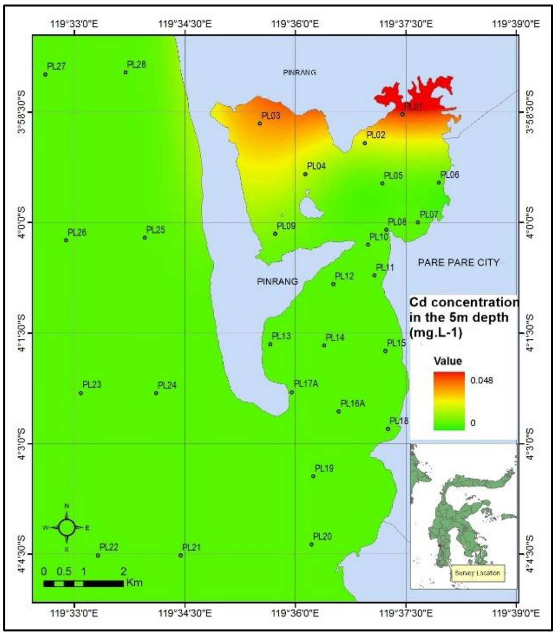

Figure 6. Cd distribution in the 5m depth

According to Waseem *et al.* (2014) Hg in the waters derived from waste activities such as industry, cosmetics, batteries and fluorescent lamps. Mercury (Hg), which is one of heavy metal elements is the most pernicious and toxic which can harm the lives of both humans and other living creatures. The impact of mercury contamination in the waters is causing mass mortality of marine biota (Lasut, 2011).

Cadmium (Cd) is only detected at station 1 and station 2. In the surface, the concentration ranged 0.034 $mg.l^{-1}$ and 0.083 $mg.l^{-1}$ respectively (Figure 5.). In the depth of 5m, the concentration ranged 0.018 $mg.l^{-1}$ and 0.048 $mg.l^{-1}$, respectively (Figure 6.). The value of Cd exceeds the quality standard established by Ministry of Environment (2014) which is 0.01 $mg.l^{-1}$ for harbor water environment, 0.001 $mg.l^{-1}$ for marine life, and 0.002 $mg.l^{-1}$ for marine tourism. Compared with previous study by Idris (2005) the level Cd in the Pare Bay ranged from 0.004-0.0352 $mg.l^{-1}$.

According to Nordic (2003) the source of Cd in the sea naturally comes from the earth's crust as the input of the beach area originating from the rivers and coastal erosion due to the wave activity, the input from geological activities such as sea volcanoes, and the input from the air coming from the atmosphere as particles of dust. Cd also can be derived from human activities, such as disposal waste due to anthropogenic activity (household waste), and marine transportation and ship reparation activities. It was alleged that the activities within Pare Bay donates most of these metals in seawater such as marine transport, ship repair, household waste, agricultural activities, industrial emissions and smelting Zn and Pb.

According Rompas (2010), the intake of Cd from various activities on the marine environment is rapidly absorbed by aquatic organisms in the form of

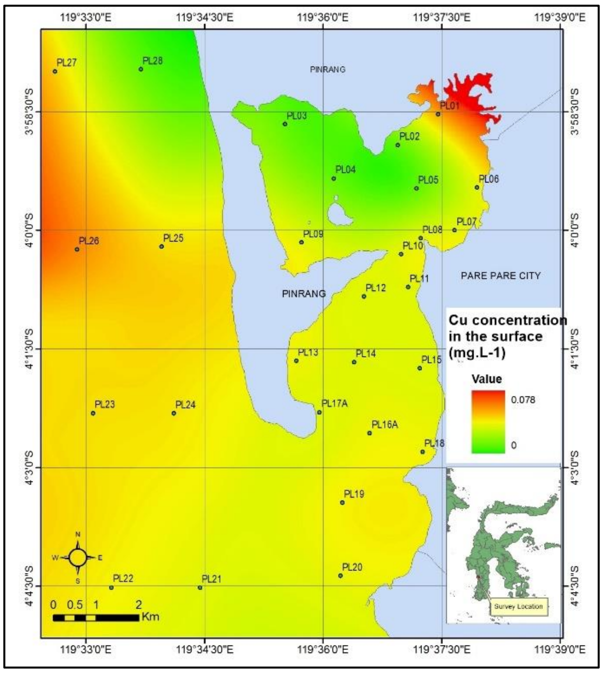

Figure 7. Cu distribution in the surface

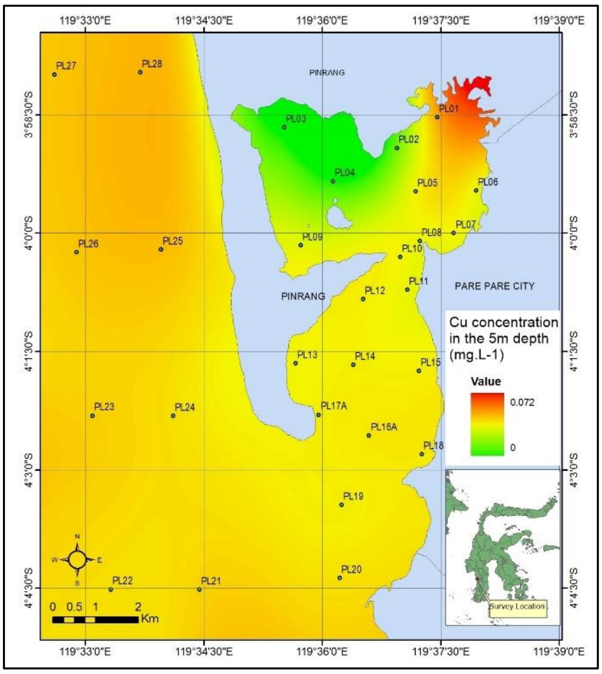

Figure 8. Cu distribution in the 5m depth

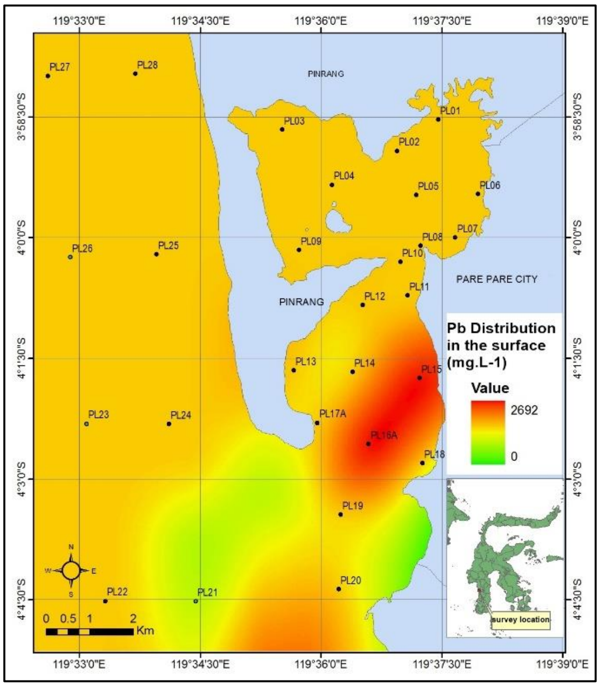

Figure 9. Pb distribution in the surface

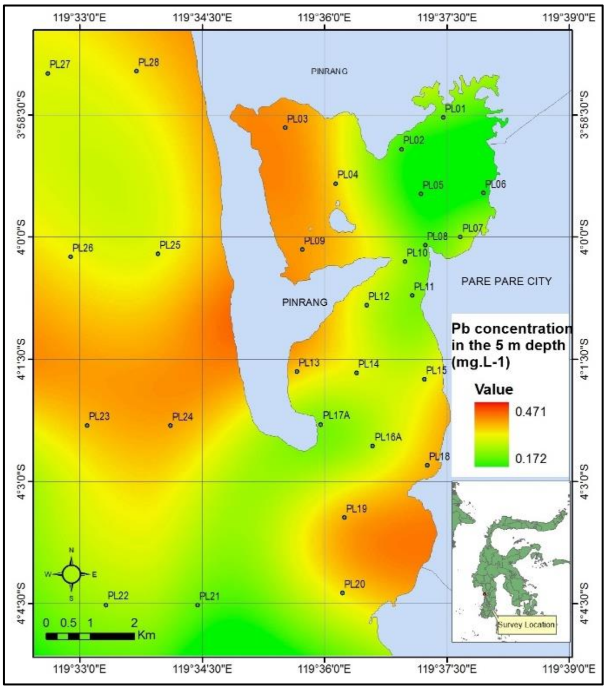

Figure 10. Pb distribution in the 5m depth

free ions (Cd^{2+}). It is associated with chloride ions (Cl), at pH 7.0 with percentage of $CdCl_2$ (51%), $CdCl^+$ (39%), $CdCl^{3+}$ (6%) and complex Cd^{2+} approximately 2.5% of the total concentration. According Usman *et al.* (2013) Cd concentration within Pare bay waters ranged from 0.6570-0.9425 $mg.l^{-1}$. The high concentration of Cd might be caused by the amount of domestic waste generated by traditional markets.

The minimum concentration of copper (Cu) in the surface reached 0.043 $mg.l^{-1}$ which is identified at stations 12, 15 and 17. While, the maximum Cu reached 0.078 $mg.l^{-1}$ which is identified at station 1 (Figure 7.). In the depth of 5 m, the minimum Cu reached 0.043 $mg.l^{-1}$ which is identified at station 8 and 11. The maximum concentration is observed at the station 1 reached 0.072 $mg.l^{-1}$ (Figure 8.).

According to the standard quality established by Ministry of Environment (2014), the value of Cu slightly exceeds the standard that supposed to be equal to 0.05 $mg.l^{-1}$ for port and maritime tourism. Whilst the value surpasses the standard for marine life that is equal to 0.008 $mg.l^{-1}$. It is widely perceived that the distribution of dissolved copper is adjacent to the northeast of the observation area. In the west part outside Pare Bay, Cu concentration is tremendously low. At a depth of 5 m, Cu concentration is higher than in the surface layer.

According to Idris (2005) Cu content within the Pare Bay ranged from 0.13 up to 0.39 $mg.l^{-1}$. It shows that Pare Bay receives input waste containing Cu. The location closest the marine activity zone in the port of Pare Bay is the source of metals. According to Rochyatun *et al.* (2010) Cu contained in various paint of the ships that serves as an anti-rust paint or anti-fouling. Cu probably derived from the dye on the ship. These materials contain Pb in the form of compounds such as $PbCO_3$ or Pb white and Pb_3O_4 which is useful in the manufacture of paints (Palar, 2004).

At some observation stations in the surface layer, dissolved Zn cannot be observed such as at stations 13 and 17, stations 20, 22 and 24. Zn concentration ranged from 0.004-0.112 $mg.l^{-1}$ (Figure 11.). In the depth of 5 m (Figure 12.), Zn concentration ranged from 0.007-0.098 $mg.l^{-1}$. The maximum value of Zn is approaching the quality standard established by Ministry of Environment (2004) that is equal to 0.1 $mg.l^{-1}$ for port environment and 0.095 $mg.l^{-1}$ for aquatic marine tourism, while the designation of marine water quality is equal to 0.05 $mg.l^{-1}$.

Compared to the previous study by Ardiyanti (2005) Zn content measured within Pare Bay ranged from 0.0263-0.0744 $mg.l^{-1}$. According Meilanty activity of the pier, fishing transport and shipbuilding. According to Slukovskii and Polyakova (2017) Cu is used in wood preservatives and anti-rust paint on the hull. High levels of Cu in the water can potentially kill the fish (Lestari and Edward, 2004).

Figure 9 shows the distribution of lead (Pb) in the Pare Bay waters. Pb concentration ranged from 0.111-2,692 $mg.l^{-1}$. In the depth of 5 m (Figure 10) Pb concentration ranged from 0.172-0.471 $mg.l^{-1}$. Pb concentration exceeds the quality standard established by the Ministry of Environment (2014) that is 0.05 $mg.l^{-1}$ for port and maritime tourism. Moreover, Pb concentration endangers the marine life due to its concentration tremendously high (>0.008 $mg.l^{-1}$).

Pb is one of heavy metals that is a major concern in terms of health, because of its impact on a large number of human toxicities, environment pollution, and hazardous toxic properties (Yusuf *et al.*, 2005). Pb triggers a high toxicity to human which it can impair the brain development on children, blockage of red blood cells, anemia and other limbs. It potentially can be accumulated directly on the marine organisms which may be daily consumed by human (Purnomo, 2009).

According Ardiyanti (2005) Pb metal content measured in the Pare Bay ranged from 0.0373 up to 0.1947 $mg.L^{-1}$. According Meilanty (2005) high concentration of Pb in the Pare Bay waters is caused by a freighter that is always active on the site. Thus, the release of Pb is triggered by the use of fuel and fuel waste disposal of larger engine in the study area. Other than that, it is caused by the activities of people who live around the port that uses paint as a (2005) Zn waste comes from the pipes oil flow. It is also coated with a mixture of metallic zinc to prevent the corrosion. The existence of a wide variety of domestic garbage in the surrounding waters within the bay also triggers heavy metals enhancement. It will automatically cause environmental pollution.

Water quality data observed such as pH, salinity and temperature were measured at the same time of sampling (Table 2.). The temperature still within the range existed in the Indonesian waters ranging from 28-31°C (Monoarfa, 2002). The acidity level triggers the deposition of heavy metals in the water. The higher the pH value, the easier the dissolved metals to be accumulated. pH values ranged from 7.47-7.93. This value is still within the normal range for seawater ranging from 5.6 to 8.3 (Wahab and Mutmainnah, 2005). Compared to previous study by Meilanty *et al.* (2005) the degree of acidity (pH) in the Pare Bay waters ranged from 7.4 to 7.5 which is still feasible for marine life.

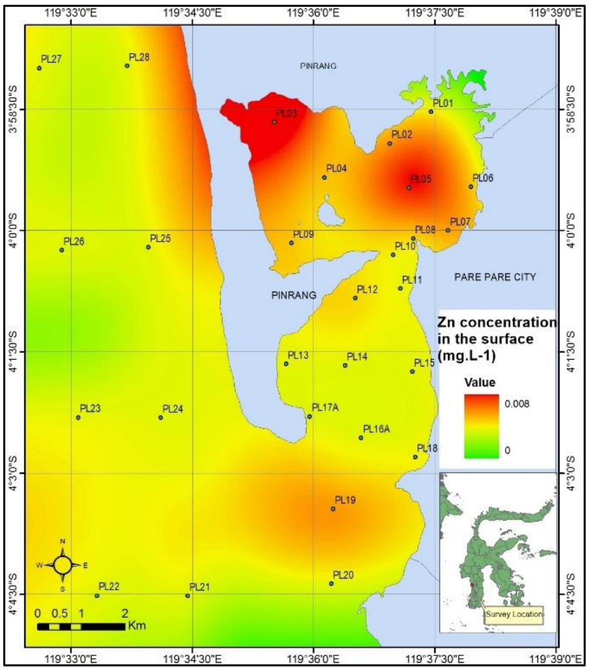

Figure 11. Zn distribution in the surface

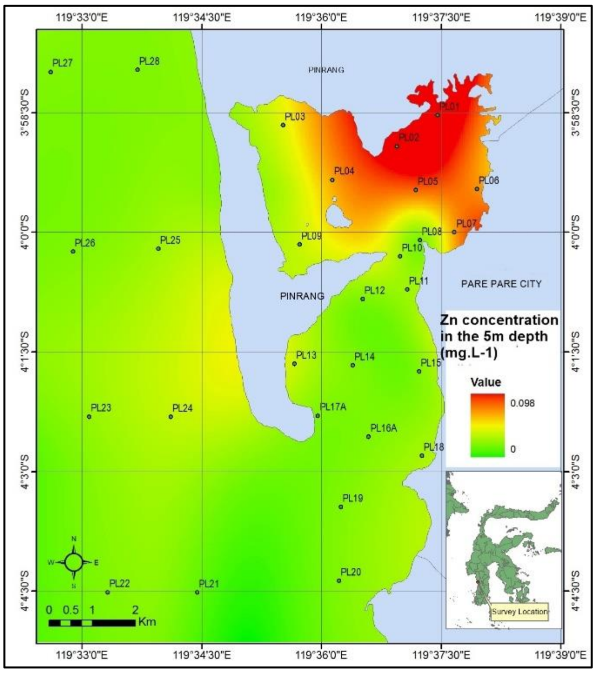

Figure 12. Zn distribution in the 5m depth

Temperature is one of the physical factors which is very important in aquatic environment. Changes in water temperature will affect the other physical, chemical, and biological parameters (Hala *et al*., 2013). The temperature ranged from 27.2-28.6^{o}C within Pare Bay and surrounding. It is lower than the previous study by Meilanty (2005) the temperature ranged between 31-32^{o}C. The temperature condition is not suitable for aquatic biota. According to Hala *et al.* (2013) the temperature of Pare Bay ranged from 29-32^{o}C. The raising temperature will trigger the heavy metal toxicity in the waters.

Salinity is the total weight of all salt (in grams) dissolved in one liter of water. Based on the observation, salinity value ranged from 31.73 up to 32.9 $^o/_{oo}$. It is lower than the previous study by Hala *et al*. (2013) salinity value ranged from 32.5 up to 33 $^o/_{oo}$. Salinity also affects the presence of heavy metals in water. The lower the salinity value, the greater the toxic level of heavy metals (Yudiati *et al.*, 2009).

Conclusions

Heavy metal concentrations generally exceed the standard for marine biota. It potentially can harm the marine life and reduce the function value of Pare Bay as a center of maritime. The high value of heavy metals can increase the toxic level in the territorial waters, where the consumption of water for activities in the coastal depended on the Pare Bay. Heavy metals content in the surface and in the 5m depth are slightly different. In the deeper layer, heavy metal concentrations tend to be higher because of the natural behavior of heavy metals that tend to be deposited in the bottom. The water quality parameters such as pH, temperature, and salinity contribute to the toxicity enhancement of heavy metals in the Pare Bay.

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References

Ardiyanti, A. 2005. Analisis Kandungan Logam Berat Timbal (Pb) dan Seng (Zn) pada Air Laut di Sekitar Perairan Pelabuhan Pare-Pare dengan Metode Adisi Standar. *J. Kimia*. 3(1): 28-33.

Darmono, D. 1995. Logam dalam Sistem Biologi Makhluk Hidup. Universitas Indonesia. Jakarta.

Departemen Kelautan dan Perikanan. 2008. Laporan Monitoring Kualitas Ikan dan Lingkungan Kawasan Budidaya di Provinsi Sulawesi Selatan, DKP Takalar.

Fitriani, A.N., Daud, A. & Ruslan, R. 2014. Studi Konsentrasi Logam Berat Timbal (Pb) dalam Sedimen dan Udang di Perairan Sungai Pangkajene Kabupaten Pangkep. *J. Kesehatan Lingkungan*. 3(1): 98-109.

Hala, Y., Syahrul, M., Suryanti, E., Taba, P. & Soekamto, N.H. 2013. Biasorption of Zn^{2+} And Cd^{2+} in A Two–Metal System By *Nannochlorop sis salina. Eur.Chem. Bull*. 2(5): 238-241. doi: 10.17628/ecb.2013.2.238-241

Idris, F. 2005. Analisis Kandungan Logam Berat Tembaga (Cu) dan Kadmium (Cd) Pada Air Laut di Sekitar Perairan Pelabuhan Pare-Pare dengan Metode Adisi Standar. *J. Kimia*. 3(1): 33-39.

Johnson, K. & McChow, J. 2001. Using ArcGIS spatial analysis. *Environmental Systems Research Institute (ESRI)*, Inc, USA. 236 pp

Johnston, C.A., 1998. Geographic information systems in ecology. Methods in Ecology. Blackwell Science. 239p.

Lasut, M. 2011. Penurunan Kualitas Lingkungan Akibat Aktivitas Tambang. Aksara Karunia. Jakarta.

Lestari, L. & Edward, E. 2004. Dampak Pencemaran Logam Berat Terhadap Kualitas Air Laut dan Sumber Daya Perikanan (Studi Kasus Kematian Masal Ikan-Ikan di teluk Jakarta). *J. Makara Sci*. 8(2): 52-58. doi: 10.7454 /mss.v8i2.414.

Maslukah, L. 2007. Konsentrasi Logam Berat (Pb, Cd, Cu, Zn) Terlarut Dalam Seston dan Dalam Sedimen di Estuari Banjir Kanal Barat, Semarang. *J. Sumber Daya Perairan*. 2(1): 1-4.

Meilanty, H., Wahab, A.W. & Hala, Y. 2005. Analisis Kandungan Ion Timbal dan Seng pada Kerang Darah (*Anadara granosa*) di Perairan Pelabuhan Pare-pare. *J. Marina Chimica Acta*. 6(2): 12-16.

Ministry of Environment. 2004. Baku Mutu Air Laut untuk Perairan Pelabuhan. Kementerian Lingkungan Hidup. Indonesia.

Monoarfa, W. 2002. Dampak Pembangunan Bagi Kualias Air di Kawasan Pesisir Pantai Losari Makassar. *J. Sci. Technol.* 3(3): 37-44.

Nordic, N. 2003. Cadmium Review. Denmark: Prepared by COWI A/S on Behalf of the Nordic Council of Ministers.

Palar, H. 2004. Pencemaran dan Toksikologi Logam Berat. Rineka Cipta. Jakarta.

Radiarta, I.N. 2013. Hubungan Antara Distribusi Fitoplankton dengan Kualitas Perairan di Selat Alas, Kabupaten Sumbawa, Nusa Tenggara Barat. *J. Bumi Lestari*. 13(2): 234-243.

Rochyatun, E., Kaisupy, M.T. & Rozak, A. 2010. Heavy Metallic Element Distribution in Cisadane River Estuary's Water and Sediment. *Makara J. Sci*. 10(1):35-40. doi: 10.7454/mss. v10i1.151.

Rompas, R.M. 2010. Toksikologi Kelautan. Jakarta: Sekretariat Dewan Kelautan Indonesia.

Slukovskii, Z.I. & Polyakova, T.N. 2017. Analysis of accumulation of heavy metals from river bottom sediments of the urban environment in the bodies of oligochaetes. *Inland Water Biology.* 10 (3):315-322. doi: 10.1134/s1995082970 30154.

Supardi, I.R., Ramang, L.M. & Bahar, R. 2014. Analisis Pb dalam Beberapa Jenis Ikan dari Perairan Suppa Kabupaten Pinrang. *J. Matematika & Sains*. 2(1):26-31.

Usman, S., Ramang, L.M. & Nafie, N.L. 2013. Distribusi Kuantitatif Logam Berat Cd dalam Air, Sedimen dan Ikan Merah (*Lutjanus erythopterus*) di Sekitar Perairan Pelabuhan Parepare. *J. Mar. Chimica Acta.* 14(2): 49-55.

Wahab, A.W. & Mutmainnah, M. 2005. Analisis Kandungan Logam Berat Timbal dan Seng DI sekitar Perairan Pelabuhan Pare-Pare dengan Metode Adisi Standar. *J. Mar. Chimica Acta*. 6(2): 21-24.

Waseem, A., Arshad, J., Iqbal, F., Sajjad, A., Mehmood, Z. & Murtaza, G. 2014. Pollution status of Pakistan: a retrospective review on heavy metal contamination of water, soil, and vegetables. *BioMed Res. Int.* 813206:1-29. doi: 10.1155/2014/ 813206

Yudiati, E., Sedjati, S., Enggar, L. & Hasibuan, I. 2009. Dampak Pemaparan Logam Berat Kadmium pada Salinitas yang Berbeda terhadap Mortalitas dan Kerusakan Jaringan Insang Juvenile Udang Vaname (*Litopeneus vannamei). Ilmu Kelautan.* 14(4): 29-35. doi: 10.14710/ik. ijms.14.4.29-35.