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Heavy Metal Concentrations of Chromium (Cr) and Copper (Cu) Based on Particle Size and Sediment Depth Variation in Paotere Port Waters, Makassar

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ABSTRAK

Analisis kandungan logam berat Cr dan Cu berbagai ukuran partikel sedimen di perairan Pelabuhan Poatere Makassar telah dilakukan. Sampel sedimen diambil dengan menggunakan pipa polietilen yang panjangnya 30 cm. Sampel diayak menggunakan ayakan mekanik ukuran 1000, 250 dan 63 µm. metode analisis yang digunakan adalah AAS (*Atomic Absorption Spectroscopy*) yang diawali dengan penambahan HNO_3 lalu didestruksi menggunakan *microwave*. Sebaran ukuran partikel sedimen permukaan pada perairan Pelabuhan Paotere yaitu untuk ukuran partikel 250 – 1000, 63 – 250 dan 63 µm berturut-turut adalah 36,04%; 29,51% dan 10,07%. Ukuran partikel sedimen berbanding terbalik dengan konsentrasi logam berat. Konsentrasi Cu dalam sedimen berukuran 63 µm adalah 141,55 mg/kg; 250 µm adalah 56,52 mg/kg dan 1000 µm adalah 51,50 mg/kg. Konsentrasi Cr dalam sedimen berukuran 63 µm adalah 36,68 mg/kg; 250 µm adalah 18,65 mg/kg dan 1000 µm adalah 8,78 mg/kg. Konsentrasi logam semakin kecil seiring dengan bertambahnya kedalaman sedimen. Konsentrasi Cu dalam sedimen kedalaman 0 - 10 cm adalah 93,46 mg/kg; 10 - 20 cm adalah 77,51 mg/kg dan 20 - 30 cm adalah 76,28 mg/kg. Konsentrasi Cr dalam sedimen kedalaman 0 - 10 cm adalah 22,04 mg/kg; 10 - 20 cm adalah 21,68 mg/kg dan 20 - 30 cm adalah 20,87 mg/kg.

Kata kunci: AAS, kromium, paotere, sedimen, tembaga

INTRODUCTION

South Sulawesi province is one of the centers of economic activity in the eastern part of Indonesia so that South Sulawesi into the gate area . One of the existing ports in the port of Makassar is Paotere. Cargo ships and passenger out of the port each time and will tend to increase every year according to the current conditions of the earth's population needs. Increasing the volume number of the vessel wastewater containing oil (oily waste) is also likely to increase, causing pollution Pollution is waste if it is not treated immediately will damage the environment in the waters around the port. Chemical substances into water bodies will eventually settle in the sediment. Sediment is considered as the most important part of aquatic ecosystems because it is the site of biogeochemical cycles and are the basis of food webs (Sunardi and Ariyanti, 2009). Physical aspects of sediment consisting of particles that can be found in the form of coarse sand, fine sand and mud. Based on research conducted by the Sahara (2009), the smaller the particle size of the sediment , heavy metal content increases. Relation to the depth of sediment heavy metal concentrations also need to be considered. Chromium including heavy metals with considerable impact and dangers to watch out for. Chromium (VI) in waters is highly toxic, corrosive, carcinogenic and has a very high solubility. Copper with the chemical name cuprum denoted by Cu . Copper (II) in a small amount is needed by the body for the formation of red blood cells, but large amounts can motivate bad taste on the tongue. Widespread systemic poisoning can damage the fibers of the blood (capillaries), kidney damage, central nervous and followed by depression. If poisoning in small amounts continuously. Pigmentary cirrhosis can lead to liver (liver hardened) (Hidayati and Yusrin, 2008). Referring to this, the research will be carried out on the levels of heavy metals in particular Cr and Cu by particle size and depth of sediment in the waters of Port Paotere environment.

METHODS

Materials

The materials used in this study is that sediment samples taken randomly in the waters of Port Paotere, HNO_3 pa, $K_2Cr_2O_7$, $Cu(NO_3)_2.3H_2O$, aquadest and aquabidest.

Tools

The tools used in this study are the tools that are common in laboratory glassware, GPS, polyethylene pipe, Spektrofometer Atomic Absorption and storied sieve size of 63, 250 and 1000 µm stainless steel.

PROCEDURE

Sampling

Sampling was carried out at 4 stations around the study area by taking sediment at three depths ie 0-10 cm, 10-20 cm, and 20-30 cm (from the sediment surface).(Siaka,1998).

Station I: Complex Fishermen.
Station II: TPI and estuaries Tallo.
Station III: The waters off.
Station IV: The shipyard.

Sampling was done using polyethylene pipe. efore use, the pipe and polyethylene bottles soaked in 10% HNO_3 for not less than 24 hours, then rinsed several times with distilled water. Once sampling is complete, the samples obtained put in polyethylene containers, then samples were kept in an ice box and immediately transported to the laboratory (Astuty, 2011). Samples were stored in a refrigerator (4 °C) before sieving. Seawater also taken place sediment sampling to assist in the screening process. This is done to make the same condition as at the sampling sites (Agustinawati, 2001).

Sieving Sediment Samples

Sediment fraction analysis performed using a mechanical sieve each has a size of openings in 1000, 250, and 63 µm. The method used is the wet sieving. In this method of grains of sediment are classified by Wentworth Scale (Wibisono, 2005). Early stages of sediment grain size analysis of sediment samples are transported in containers to dry. Dried sediment was weighed and soaked with distilled water until the water together with the sample. Sediment samples were subsequently poured into the sieve and the results of sieve fractions were separated by the different grains of coarse sand 250 - 1000 µm, soft sand 63-250 µm, and mud <63 µm. Sediment grain fraction which has been moved into a separate container to be dried again. Samples were dried and then weighed according to the sieve openings (Astuty, 2011).

$$\text{Fraksi (\%)} = \frac{\text{Berat kering setelah diayak}}{\text{Berat kering sebelum diayak}} \times 100\%$$

Sample preparation

The dried sediment samples crushed and pounded until smooth and weighed 0.5 grams and then inserted into the tube vessel. Added by 10 mL HNO_3 p.a. Destruction of samples with using the microwave. After the sample was cooled to room temperature. Destruction results filtered with Whatman paper No.. 41 into a 50 mL volumetric flask and add distilled water up to the mark. Then

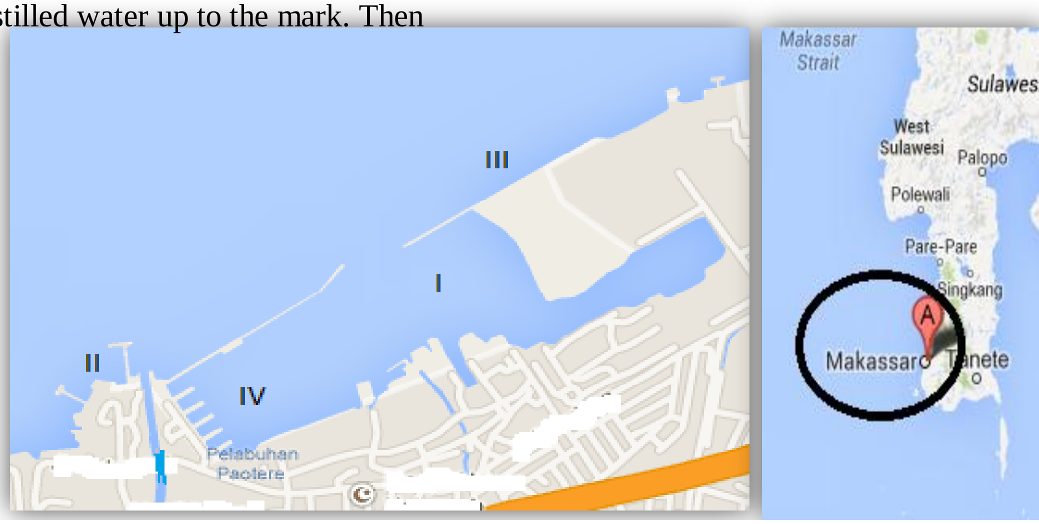


Figure 1. Sampling Map

we measured the concentration of heavy metals using AAS (Astuty, 2011).

Determination of heavy metals

<u>Calibration curves making</u>

Calibration curve was made by measuring the absorbance of a series of concentrations of standard solutions that have been created, then made a graph showing the relationship between the absorbance with the concentration of the standard solution.

<u>Determination of Metal Concentrations</u>

Determination of Cr and Cu concentrations in the samples was done by using a calibration curve linear line, so that the concentration of the sample can be determined from the measured absorbance. After measuring the concentration is known, then the actual concentration of Cr and Cu in dry samples can be determined by calculating:

$$M = \frac{C\ V\ F}{B}$$

wherein:

M: The concentration of metals in the sample (mg / kg),

C: concentration obtained from the calibration curve (mg / L),

V: volume of the sample solution (L),

F: dilution factor, and

B: Weight of the sample (kg)

RESULTS AND DISCUSSION

Results of in situ measurements of parameters

Table 1. Results Analysis of In Situ Parameters Each Station

Stations	Parameters					
	Temp. (ºC)	pH	Salinity (ppt)	DO (mg/L)	TDS (g/L)	TSS (mg/L)
I	29	8	31,3	1,30	181,8	0,0
II	29	7	26,7	1,53	155,0	1,0
III	28	7	27,1	1,38	156,0	0,0
IV	28	8	27,1	0,32	158,0	1,0

Fractions Sediment Particle Size

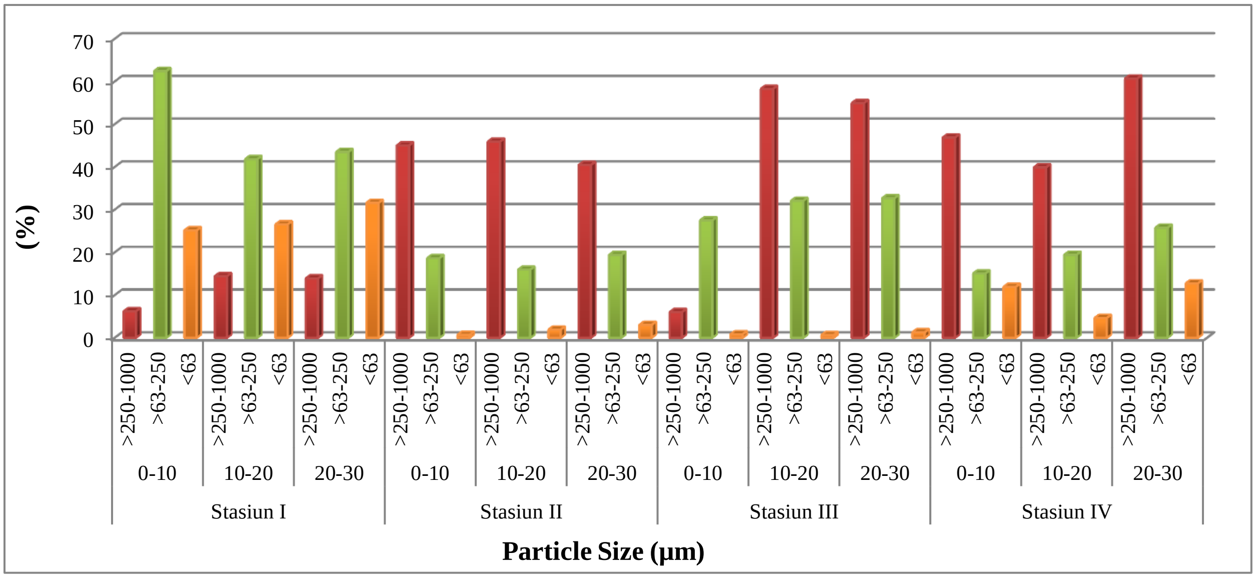
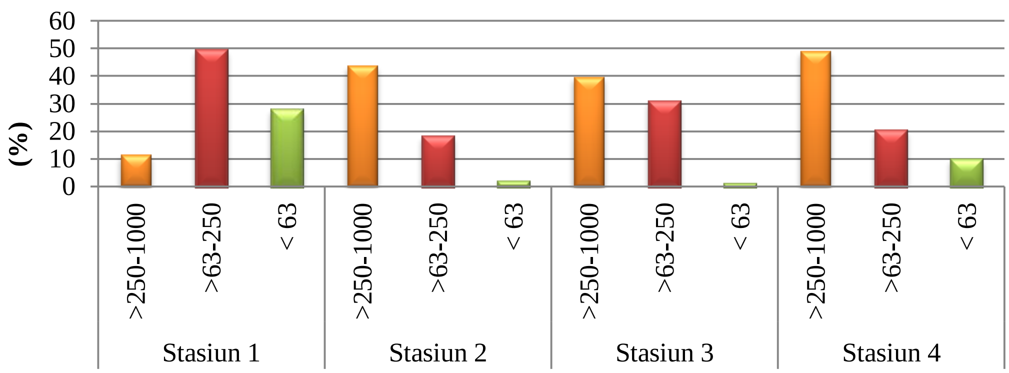


Figure 2. Histogram Fraction Sediment Particle Size Distribution in Different in Different Depth Depth Each station (%)

Sediment particle size fractions in different depths of each station can be seen on the histogram as shown in Figure 2. The result is that the particle size distribution is the most common particle size 250 µm at the first station with a depth of 0-10 cm, which is about 62,45% and the percentage distribution of particle size is at least 63 µm sized sediment at station III with a depth of 10-20 cm, which is only about 0,63%.

Distribution of the average particle size of each station at a depth of 0-30 cm



Particle Size (µm)

Figure 3. Sediment Particle Size Distribution Histogram average Each station on the depth 0-30 cm

Sediment particle size distribution histogram of the average shown in Figure 3 is very varied because it is caused by several things. Physically, sediment grain size of each station is different. Referring to the classification of sediments based on Wentworth scale (Wibisono, 2005) sediments at station I include coarse silt, sediment at station II and III include coarse sand, while the sediment at station IV is fine sand. It is influenced by sampling site. Grain sediments at station I look more refined than the grains of sediment at station IV and grain sediments at station II and III because of the distance, the outskirts of the port to the station I and IV as far from the outskirts of the port to the station II and III. The movement of sediment in the waters affected by the turbulence that occurs in the body of water itself, the ups and downs in the vicinity of the beach and the breakwater structures (Romdania, 2010). At station II, III and IV are the foundation of human-made surroundings that is more shallow than the station I. That is why the grain size of the sediment at station I is more subtle than the three other stations.

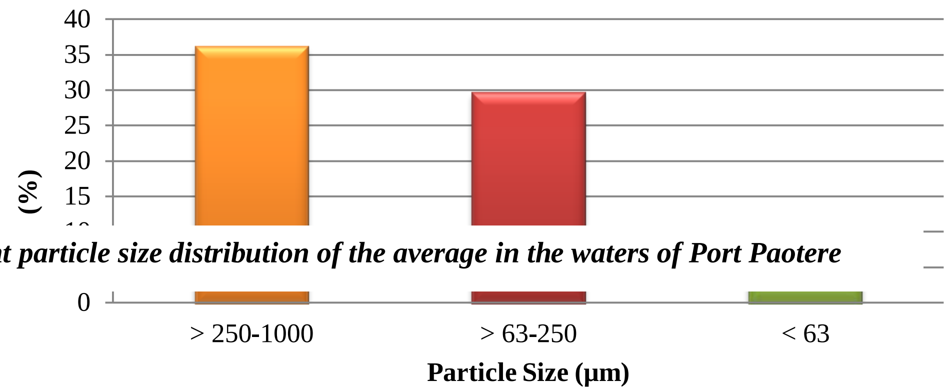


Figure 4. Sediment particle size distribution histogram of the average in the harbor waters Paotere

Sediment particle size distribution histogram of the average in the waters of Port Paotere obtained from four stations are shown in Figure 4. The average value of sediment particle size > 250 - 1000 µm was 36,04%; particle size > 63-250 µm was 29,51% and a particle size <63 µm was 10,07%. The percentage distribution of sediment particle size on high Paotere harbor waters on particle size > 250–1000 µm. This may be caused by sediment sampling sites tend to be rather close to the edge of the harbor and building foundations so that the average man sediment grain size obtained relatively large.

Figure 6. Histogram analysis of Cu concentrations (mg / kg) on average particle size of sediment

Analysis of Cu concentrations (mg / kg) of sediment particle size (lm)

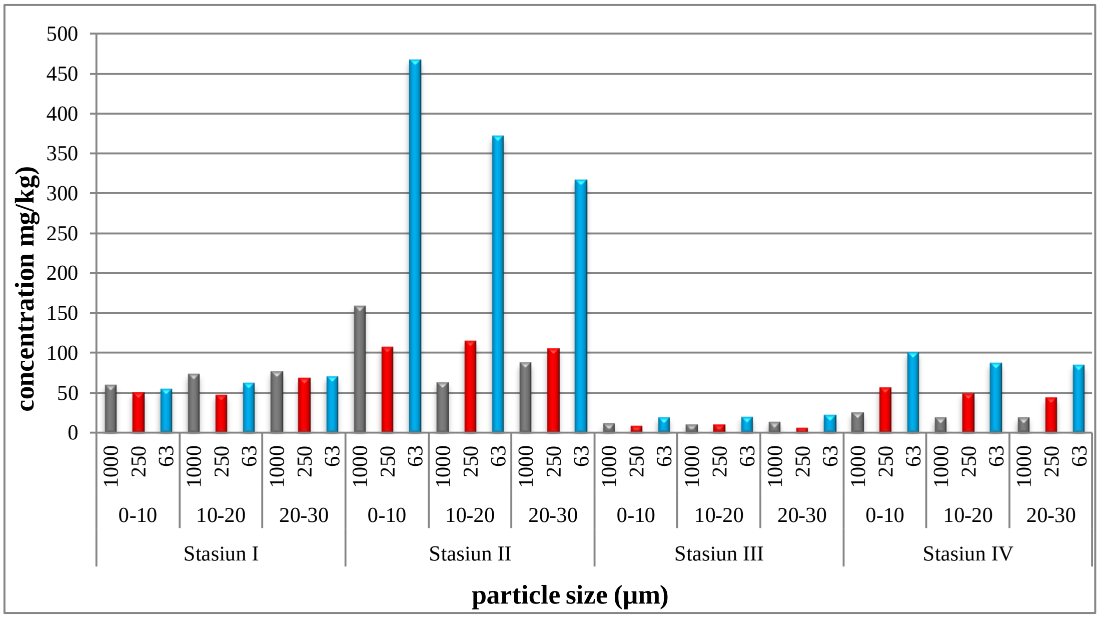


Figure 5. Histogram analysis of Cu concentrations (mg / kg) particle size of sediment

Results of analysis of heavy metals Cu sediment particle sizes vary widely. Based on the histogram shown in Figure 5, the concentration of Cu highest around 467,89 mg / kg found in sediment samples II station measuring 63 µm depth of 0-10 cm. While the lowest concentration of Cu is only about 6,49 mg / kg in sediment measuring station III 250 µm depth of 20-30 cm.

Results of analysis of Cu concentrations (mg / kg) the average particle size of sediment

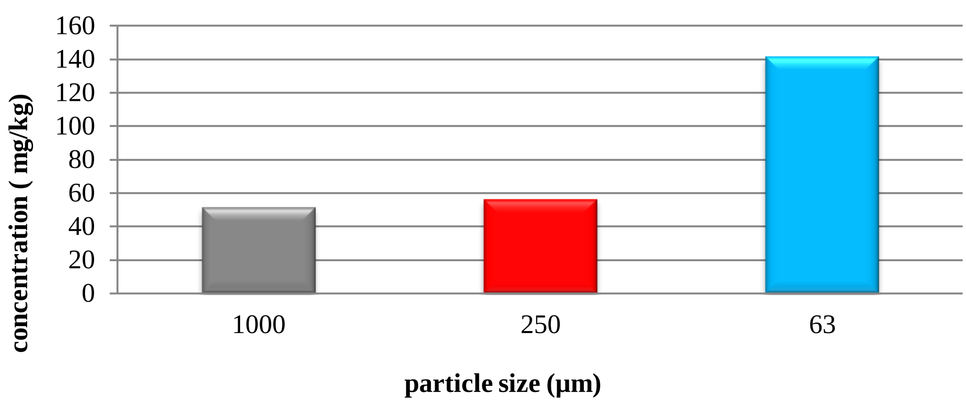


Figure 6. Histogram analysis of Cu concentrations (mg / kg) on average particle size of sediment

Content analysis of Cu results on average in a range of sediment particle size indicated by the histogram in Figure 6. Concentration of Cu in sediment size of 63 µm approximately 141,55 mg/kg, The concentration of metal Cu in the sediment size of 250 µm around 56,52 mg/kg and the concentration of Cu in the sediments around 1000 µm 51,50 mg/ kg.

Results of analysis of metal concentrations of Cr (mg / kg) particle size of sediment

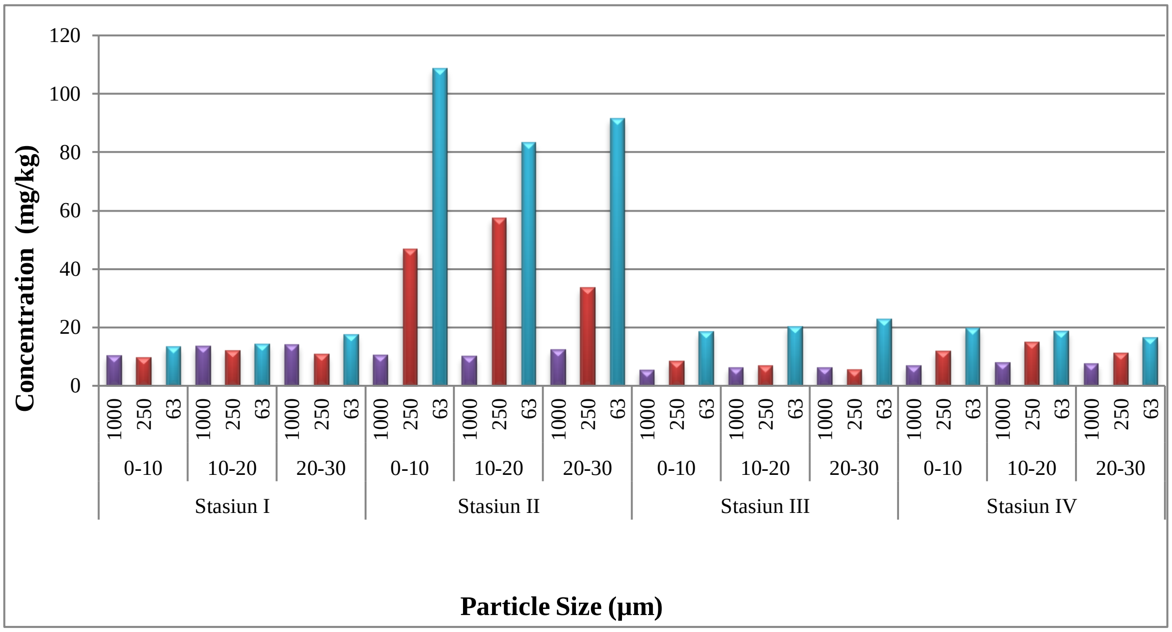


Figure 7. Histogram of analysis of metal concentrations of Cr (mg / kg) particle size of sediment

Based on the histogram in Figure 7, the concentration of Cr highest around 108,25 mg/kg found in sediment samples measuring station II 63 µm depth of 0-10 cm. While the Cr concentration of the lowest around 5,05 mg / kg found in sediment samples III stations that measure 250 µm depth of 20-30 cm. Concentrations of Cr at station III was relatively lower than the other three stations. Judging from the location of the sediment, the condition of the waters around the station III still looks clear and clean and the location is a bit far from the source of pollution.

Results of analysis of metal concentrations of Cr (mg / kg) particle size of sediment

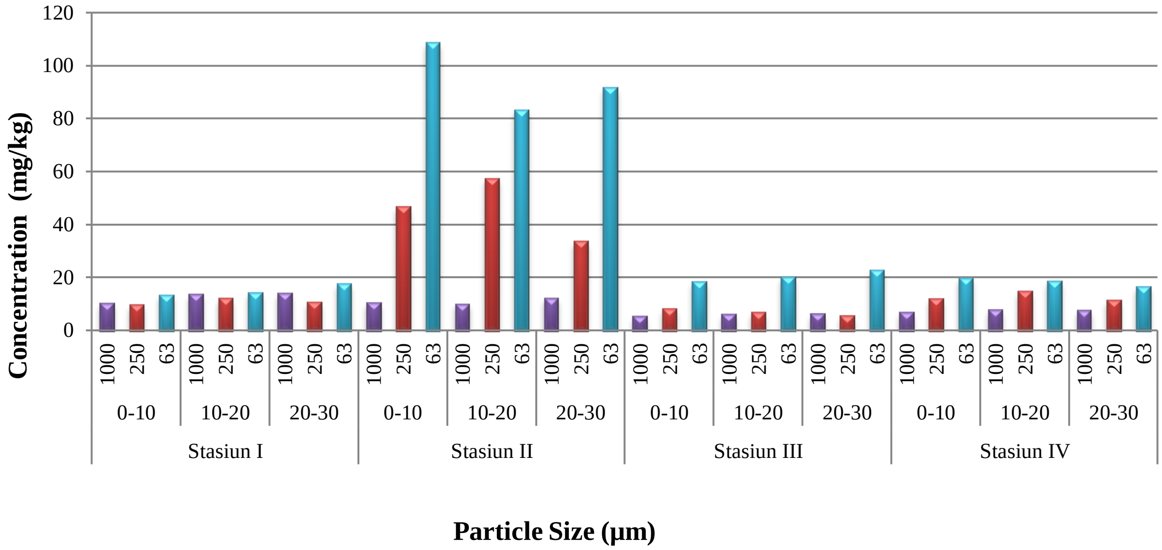


Figure 8. Histogram analysis Cr metal concentrations (mg / kg) particle size of sediment

Content analysis results of Cr metal on average in a range of sediment particle size indicated by the histogram in Figure 8. Concentrations Cr in sediment size 63 µm approximately 36,68 mg/kg, Cr metal concentrations in sediment size of 250 µm around 18,65 mg/kg and Cr concentrations in sediments 1000 µm approximately 8,78 mg/kg. Measurement results in the highest Cr concentration sediment size 63 µm compared with metal concentrations in sediment size 250 and 1000 lm. The content of heavy metals in sediments associated with grain sizes of sediment particles where there are high concentrations of heavy metals in sediments with finer particle size than the coarse sediment. And vice-versa. Fine sediments have a large surface area so it is relatively easy to bind metals (Hutabarat and Evans, 2006).

Results of analysis of Cu (mg / kg) in different sediment depth (cm)

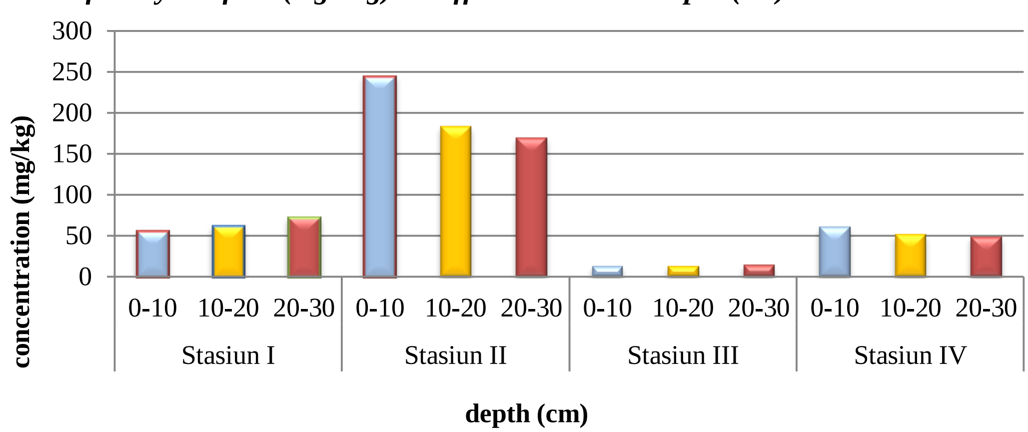


Figure 9. Histogram analysis of Cu concentrations (mg / kg) of various sediment depth (cm)

Results of analysis of Cu concentration range of depths in Figure 9 shows the variation of metal concentration each different station. Highest concentration of Cu around 244,54 mg/kg found in sediments station II depth 0-10 cm. Where is Cu concentration of the lowest around 13,09 mg/kg in sediment depth stations III 0-10 cm. Contained the highest concentration of Cu in the sediment station II. Heavy metals Cu probably derived from fishing boat anchors were lowered into the water every time the boat stopped. While on station III Cu concentration is low because satsiun rarely passed fishing boats and iron ships.

Results of analysis of Cu (mg / kg) on average in the range of sediment depth (cm)

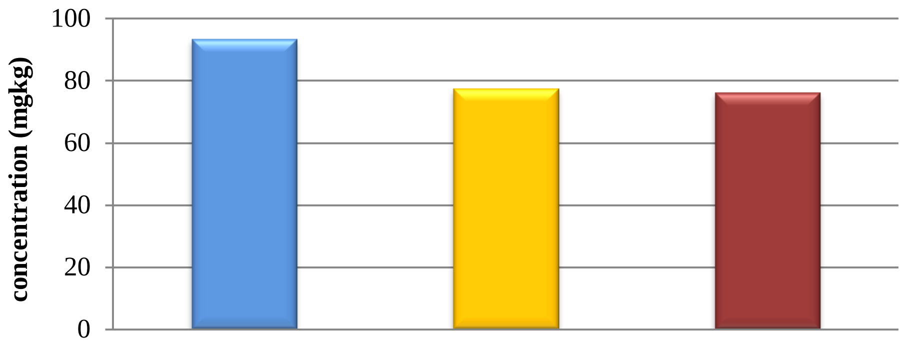


Figure 10. Histogram analysis of Cu concentrations (mg / kg) the average range of sediment depth (cm)

Content analysis results Cu on average in a range of sediment depths indicated by the histogram in Figure 10. Concentration of Cu at a depth of 0-10 cm around 93,46 mg/kg, the concentration of Cu at a depth of 10-20 cm around 77,51 mg/kg, and the concentration of Cu at a depth of 20-30 cm around 76,28 mg/kg. In general, the smaller the deeper sediment Cu metal content. Cu originating from fishing vessels anchor tends to be greater interaction with the surface sediment (depth 0-10) so that the concentration of Cu at a depth of 0-10 cm at a depth greater than 10-20 and 20-30 cm.

Results analysis Cr metal (mg / kg) in different sediment depth (cm)

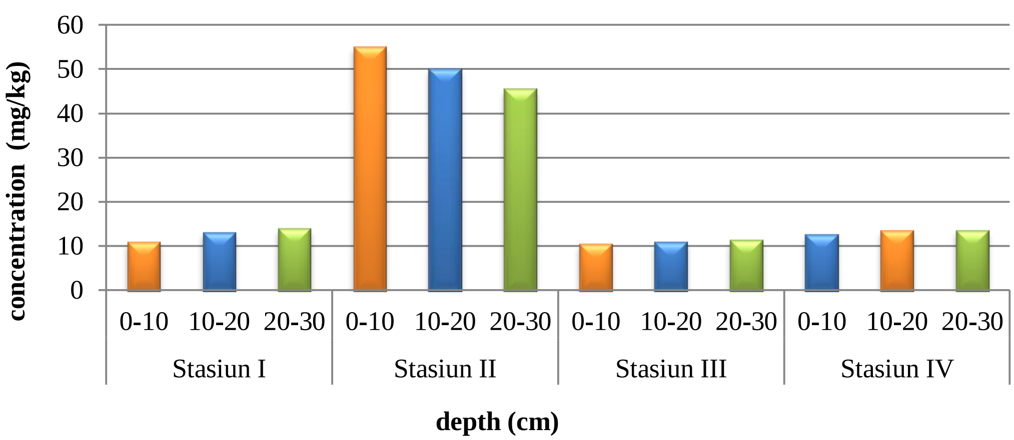


Figure 11. Histogram analysis of metal concentrations of Cr (mg / kg) of various sediment depth (cm)

Results analysis Cr concentration of various depths are shown in Figure 11. Highest Cr concentrations approximately 54,86 mg/kg found in sediments station II depth 0-10 cm. While the Cr concentration of the lowest around 10,27 mg/kg in sediment station III depth 0-10 cm. Similarly Cu, Cr concentration is highest in the lowest sediment in station II and III sediment station.

Results analysis of Cr metal (mg/kg) on average in the range of sediment depth (cm)

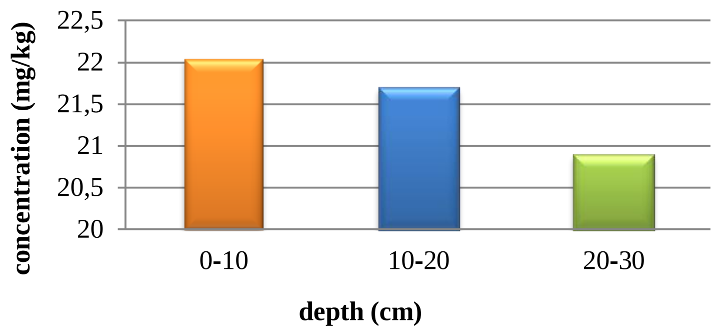


Figure 12 . Histogram analysis of metal concentrations of Cr (mg / kg) the average range of sediment depth (cm)

Results analysis content of Cr metal on average in a range of sediment depths indicated by the histogram in Figure 12 . Concentration of Cr at a depth of 0-10 cm around 22,04 mg/kg , concentration of Cr at a depth of 10-20 cm around 21,68 mg/kg , and the Cr concentration at a depth of 20-30 cm around 20,87 mg/kg. Cr dispersal patterns also decreased proportional to the increase in the depth of sediment in each location (the difference is very noticeable). Greatest concentrations found in surface sediments (0 cm depth). This might be due to the metals in the surface sediments is a relatively new metal accumulated prior to sampling carried out.

Based on sediment quality guidelines in mg/kg dry weight sediment maximum acceptable concentration of Cu was 30 mg/kg and Cr is 51 mg/kg (Febris and Werner , 1994). Results of analysis of Cu and sediment particle size analysis based on the depth of Cu, Cu concentration at station III has not been polluted than the station I, II and IV which have passed the maximum quality value Cu concentrations in the sediment. Unlike Cu , Cr analysis in various particle sizes and depths showed that only stations that have been contaminated II . Cr concentrations at stations I, III and IV are still under the maximum quality parameters Cr in sediments.

CONCLUSIONS AND RECOMMENDATIONS

Conclusion

The conclusion that can be drawn from this study are as follows:

1 . Sediment particle size distribution in the waters of Port Paotere is the particle size > 250-1000 µm was 36,04%; particle size > 63-250 µm was 29,51% and particle size < 63µm was 10,07 %.

2 . Concentration of heavy metals in different particle sizes. Cu concentrations in sediment size 63 µm was 141, 55 mg / kg ; 250 µm was 56,52 mg/kg and 1000 µm was 51,50 mg/kg . Cr metal concentrations in

sediment size 63 μm was 36,68 mg/kg; 250 μm was 18,65 mg/kg and 1000 μm was 8,78 mg/kg. The smaller the particle size of the sediment , the greater the concentration of heavy metals. Soft sediments have more surface area making it easier to bind metal dibandinkan with coarser sediments.

3 . Concentrations of heavy metals based on depth . Cu concentrations in sediment depth of 0-10 cm was 93,46 mg/kg; 10-20 cm was 77,51 mg/kg and 20-30 cm was 76,28 mg/kg. Cr metal concentrations in the sediment depth of 0-10 cm was 22,04 mg/kg; 10-20 cm was 21,68 mg/kg and 20-30 cm depth was 76,28 mg/kg. Cr metal concentrations in the sediment depth of 0-10 cm was 22,04 mg/kg; 10-20 cm was 21,68 mg/kg and 20-30 cm depth was 20,87 mg/kg. Concentrations of Cr and Cu decreased proportional to the increase in the depth of sediment . This may be caused by the metal on the surface of the sediment measured depth of 0-10 cm is a metal that accumulates relatively new when sampling is done .

Suggestion

We recommend that future studies use a variety of particle size and more depth and great to be seen clearly significant differences in the concentration levels of heavy metals.

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