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Contamination and characteristic of Ni and Cr metal on top soil from Antang landfill, Makassar City, South Sulawesi Province, Indonesia

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Abstract. Contamination and characteristic of Ni and Cr metals at the location of Antang Landfill Makassar City on topsoil have been investigated. Sample points are divided into four holes, two holes in the direction of groundwater flow (Hole A1 and Hole C1), two Hole perpendicular to groundwater flow (Hole B1 and Hole D1). Twelve samples (hole A1/3 samples; hole C1/3 samples; B1/3 samples dan D1/3 samples) were collected and analyzed using ICP-OES method, at a depth of 0 to 10 cm, 10 to 20 cm, and 20 to 30 cm respectively. This study aims to determine the characteristic of soil samples and to study the contamination of heavy metals (especially Ni and Cr) in the Antang Landfill, Makassar City, South Sulawesi Province, Indonesia. The results show that the concentration of Ni and Cr metals on Antang Landfill had spread horizontally, with varying amounts in every depth on the topsoil. The four site samplings of Landfill were hole A1, B1, C1 and D1 for each depth, containing heavy metals Ni and Cr, exceeding the threshold with exception of Cr metal for hole B1 at the depth of 10 to 20 cm and 20 to 30 cm in the range of 10 ppm (with regression value, r = 0.75), still on the threshold set by the government of the Republic of Indonesia and the directorate general of the supervision of drugs and food.

1. Introduction

Makassar City goes through very rapid development to provide an impact of increasing the amount of waste production. Along with the growing population in Makassar, garbage problem becomes more serious. Landfill for city residents of Makassar is an important requirement to create environmental comfort in the big city. The rubbish has to be transferred to the landfill every day unless the city will be full of disturbing garbage. However, the undeniable fact is that the waste landfill in several major cities has not met the criteria as a safe place for the environment. Uncontrolled Landfill is very harmful to health and can damage the environment [1, 2].

Antang Landfill, located in Antang District, is the center of all Landfill in Makassar City. In operation, Antang Landfill applies Dumping way which so potentially contaminates groundwater. Waste is stockpiled and left open daily on soil [3]. Every activity by humans produces waste and

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almost every day humans generate waste. If the waste is not properly managed, it will cause various problems such as aesthetic problems because of the odor, becomes a disease vector, and potentially disrupt the quality of the surrounding soil [4]. Trash contains both organic and inorganic pollutants. The examples of inorganic contaminants are such as Ni and Cr [5].

Sources of heavy metal contaminants on soil include metal mining and smelting, metallurgical industry, mud waste processing, war and military training, landfills, agricultural fertilizers, and electronics industries [6, 7]. Topsoil layer is the receiver of various pollutants especially heavy metals such as Ni and Cr [8]. It can be used as an indicator to measure environment quality [9]. In every activity, humans always interact with the land. The soil is formed by decomposition of rock and organic matter for years. Soil properties may vary from one to another with different composition of bedrock, climate, and other factors. Certain chemical elements occur naturally in the soil as a mineral component, but may be toxic at the particular concentration [10]. Most of the people around the Antang Landfill Makassar use dug wells as a source of drinking water. If the soil is contaminated with heavy metals, then it can also contaminate the well (ground) water. Consuming water contaminated with heavy metals will be harmful as it settles in the body.

Heavy metal is one of the natural components in the earth that cannot be degraded or destroyed. At small concentrations, heavy metals can enter the body through food, drink, and air. The heavy metals are categorized as trace minerals, minerals with a very small amount in the human body [11]. Trace elements of some heavy metals are important to manage the human body's metabolism, but it is dangerous and toxic in high concentration as it tends to be bio-accumulated. The toxicity of heavy metals in humans causes tissue damage, especially detoxifying and excretory organs (liver and kidney). Some heavy metals are carcinogenic, teratogenic, and nerve-racking that can cause behavioral abnormalities.

Antang Landfill has been used since 1995 until now (2018) with an area of 18.8 hectares. The landfill that was originally designed to be used for 10 years, but in fact, this is still in use up to now. So it is no longer able to accommodate the volume of waste in Makassar, which reached 800 tons or about 4,000 cubics per day. According to records of the Sanitation and Environment Office of Makassar, with a total population of approximately 1.3 million people, about 3,800 m^3 or equivalent to 300 tons of municipal waste has been generated every day. Whereas the maximum capacity of Tamangapa TPA is only 2,800 m^3 of municipal solid waste every day. It needs additional landfill for 1000 m^3 waste disposal, with 87% of waste is organic and 13% is inorganic, such as plastic and paper. Based on the data of the Spatial Unit and Environmental Management Unit of Makassar (2006), Antang Landfill is estimated to have 1,240,000 tons of waste organic waste disposed of since it opened [12].

Considering this fact, it can be assumed that any pollution has occurred in the area of Antang Landfill, i.e., environmental, soil, and groundwater pollution that leads to environmental sanitation and air pollution. The movement of pollutants has spread to northwest-southeast, particularly around 300 to 450 m from Antang Landfill Trash [13]. While the direction of groundwater flow in TPA Antang is the same as the slope of rock layers which is northwest-southeast [14]. This greatly impacts shallow groundwater quality. Shallow groundwater pollution by liquid waste infiltration from the landfill can also contaminate the wells of the surrounding population. This pollution has been felt by residents around the landfill, especially for those who use free groundwater as a source of drinking water [14].

This study aims to analyze the contamination and characteristics of heavy metals Ni and Cr on the topsoil around of Antang Landfill. The study is focused on how the impact of contamination and dispersion characteristics of heavy metal metals around the location of Antang Landfill Makassar City on the people's lives around the landfill [15].

2. Methods

2.1. Research Area.

The study area is administratively located in the Manggala district, Makassar City, South Sulawesi Province, Indonesia. Geographically, study area lies at the coordinate point of 119°, 29' 10" to 119°

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29’ 40” East Longitude and 5 10’ 20” to 5 10’ 40” South Latitude. The location of the study area can be seen in figure 1.

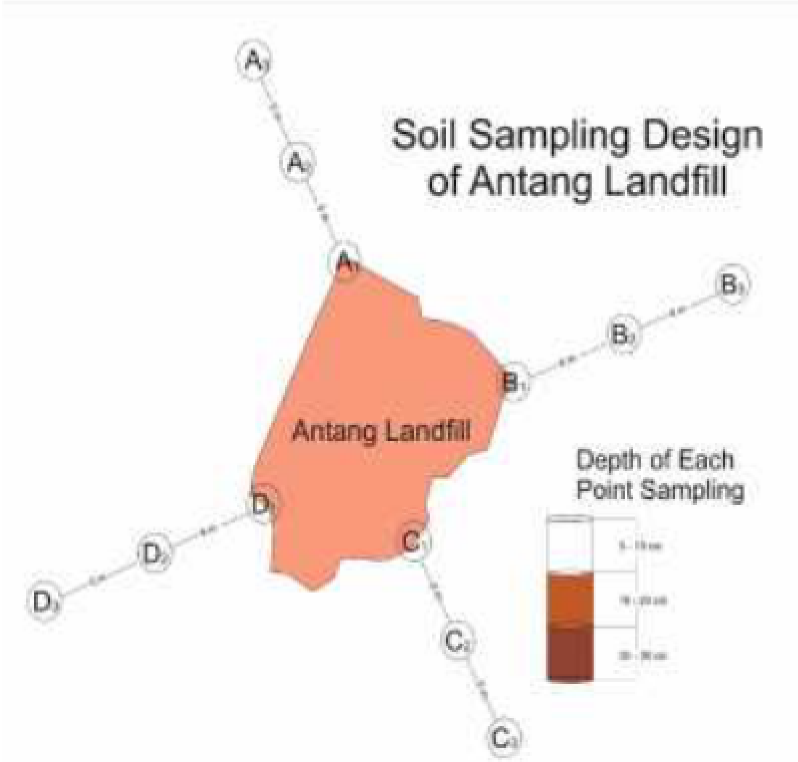

Figure 1. Location Map and Sampling Point, for Hole A1, Hole B1, Hole C1 and Hole D1, at the point of 0 m, with a depth of 0 to 10 cm, 10 to 20 cm, and 20 to 30 cm, around Antang Landfill, Makassar City, South Sulawesi Province, Indonesia.

2.2. Soil Sampling.
Soil samples in this study were collected from topsoil of Antang Landfill in Makassar City. Determination of soil sampling points were divided into 4 Holes (consist of 12 sampling), which is Hole A1 (consist of 3 samples), Hole B1 (3 samples), Hole C1 (3 samples) and Hole D1 (3 samples) at point 0 m, with depth of 0 to 10 cm 10 to 20 cm, and 20 to 30 cm respectively (see figure 1).

2.3. Soil Sampling Testing.
Before tested, the soil was baked for 48 hours at 106°C to simplify the filtering process, so the grains are not attached [7, 16, 17]. Then it was crushed by using a wooden hammer or ceramic mortar, sieved using 2- mm-stainless-steel stored in Desiccators before being analyzed [7, 15, 17, 18]. After preparation, the repaired soil sample was then sent to the laboratory for analysis.

2.4. ICP-OES Working Principle.
Soil samples are added acids, then heated and decomposed using a microwave. Then the samples are in nebulization to convert the liquid into an aerosol. After that they are dissolved to remove the solvent, thus forming the aerosol. The liquid phase of the sample is converted to a new phase by an Argon gas using a combustion generating vapor. Then the dew goes into the combustion and produces the colored atoms. The atoms are then captured by an optical atomic whose value is read and is displayed on the monitor screen of each of the metal elements of the samples [19].

3. Results and discussions

3.1 Results.
The result of heavy metal concentration Ni and Cr analysis by using ICP-OES method, for Hole A1, Hole B1, Hole C1, and Hole D1 with depth 0 to 10 cm, 10 to 20 cm and 20 to 30 cm, can be seen in (table 1). While the results of heavy metals Ni and Cr analysis for Hole A1, with a depth of 0 to 10 cm, 10 to 20 cm, and to 30 cm is represented in figure 2.

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Table 1. Result of total concentration analysis on heavy metals of Ni and Cr for Hole A1, Hole B1, Hole C1 and Hole D1 with the depth of 0 to 10 cm, 10 to 20 cm, and 20 to 30 cm, at Antang Landfill, Makassar City, South Sulawesi Province, Indonesia.

Holes	Depth (cm)	Concentration of heavy (ppm)		pH	Temperature (°C)
		Ni	Cr		
	Threshold	20	10		
A1	0-10	27	45	6	25
	10-20	28	42	5	
	20-30	28	44	6	
B1	0-10	23	11	5	28
	10-20	22	10	4.82	
	20-30	23	10	4.82	
C1	0-10	27	13	4.83	27
	10-20	22	12	4.83	
	20-30	24	12	4.83	
D1	0-10	32	53	4.83	26
	10-20	33	46	4.85	
	20-30	35	42	5	

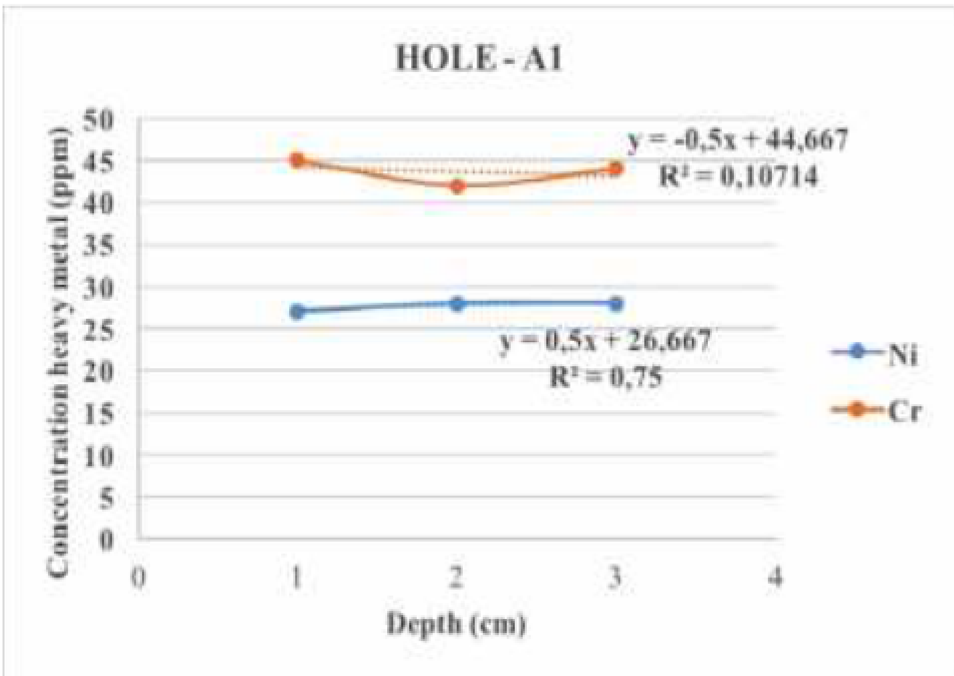

Figure 2. Graph of the analysis result of Ni and Cr heavy metal for Hole A1, at the point of 0 m with the depth of 0 to 10 cm, 10 to 20 cm and 20 to 30 cm, on Antang Landfill, Makassar City, South Sulawesi Province, Indonesia.

The concentration of Ni heavy metal on hole A1 at a depth of 0 to 10 cm is about 27 ppm, while the concentration at a depth of 10 to 20 cm and 20 to 30 cm has increased to 28 ppm respectively (see figure 2 and table 1). Cr heavy metal concentration on Hole A1 at a depth of 0 to 10 cm in the range of 45 ppm, at a depth of 10 to 20 cm the concentration of Cr decreased to 42 ppm, while the concentration at a depth of 20 to 30 cm increased again to 44 ppm.

The results of Ni and Cr heavy metals analysis for Hole B1, at the point of 0 m with a depth of 0 to 10 cm, 10 to 20 cm, and 20 to 30 cm, on the topsoil of Antang Landfill, Makassar City, South Sulawesi Province, Indonesia can be seen in figure 3 and table 1.

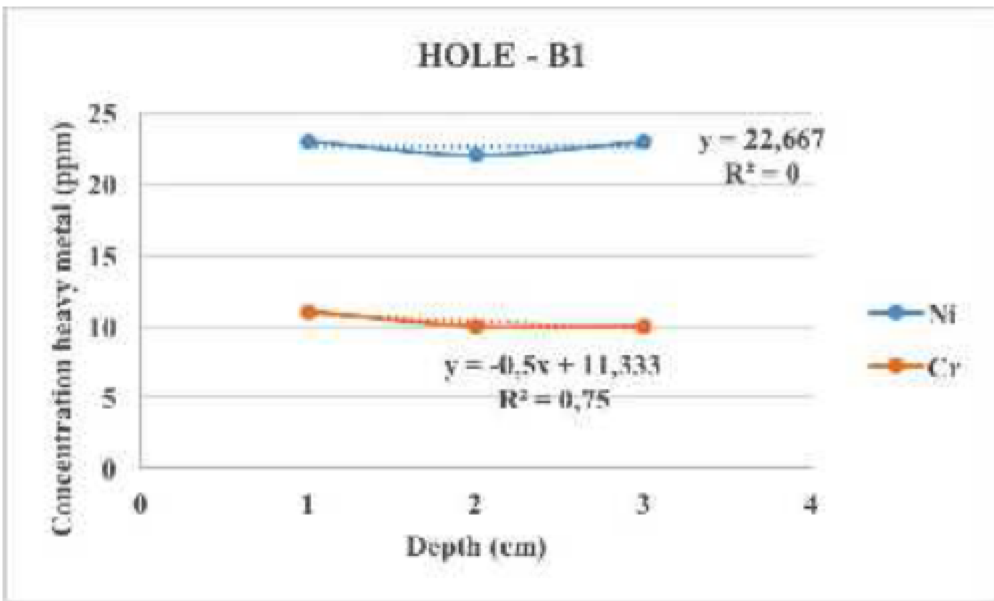

Figure 3. Graph of the analysis results on Ni and Cr heavy metal for Hole B1, at a depth of 0 to 10 cm, 10 to 20 cm, and 20 to 30 cm, in Antang Landfill, Makassar City South Sulawesi Province, Indonesia.

The concentration of metal Ni on Hole B1 at a depth of 0 to 10 cm is about 23 ppm, the concentration at a depth of 10 to 20 cm decreased to 22 ppm. On the other hand, the concentration of Ni at a depth of 20 to 30 cm increased to 23 ppm. Cr heavy metal concentration at a depth of 0 to 10 cm is 11 ppm, while concentration at a depth of 10 to 20 cm and 20 to 30 cm decrease to 10 ppm (see figure 3).

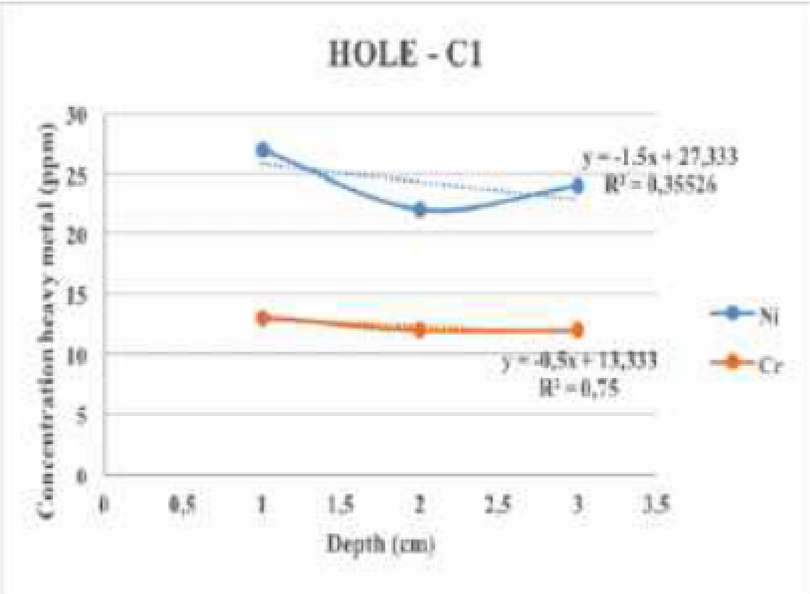

Figure 4. Graph of the analysis result of Ni and Cr heavy metal for hole C1 at a depth of 0 to 10 cm, 10 to 20 cm and 20 to 30 cm, on Antang Landfill, Makassar City, South Sulawesi Province, Indonesia.

The results of Ni and Cr heavy metals analysis for Hole C1, at a depth of 0 to 10 cm, 10 to 20 cm, and 20 to 30 cm, on the topsoil samples of Antang Landfill, South Sulawesi Province, Indonesia can be seen in figure 4 and table 1.

The highest concentration of Ni metal on Hole C1 were detected at a depth of 0 to 10 cm with a value of 27 ppm, at a depth of 10 to 20 cm the concentration decreases exponentially to 22 ppm. While the concentration of Ni in the depth of 20 to 30 cm increased to 24 ppm. Furthermore, the

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highest metal concentration of Cr is observed at a depth of 0 to 10 cm with the value of 13 ppm. The concentration of Cr at a depth of 10 to 20 cm and 20 to 30 cm the value decreases to 12 ppm respectively (table 1 and figure 4).

Moreover, the results of heavy metals Ni and Cr analysis for Hole D1, at a depth of 0 to 10 cm, 10 to 20 cm and 20 to 30 cm, on the topsoil of Antang Landfill, South Sulawesi Province, Indonesia are described in figure 5 and table 1.

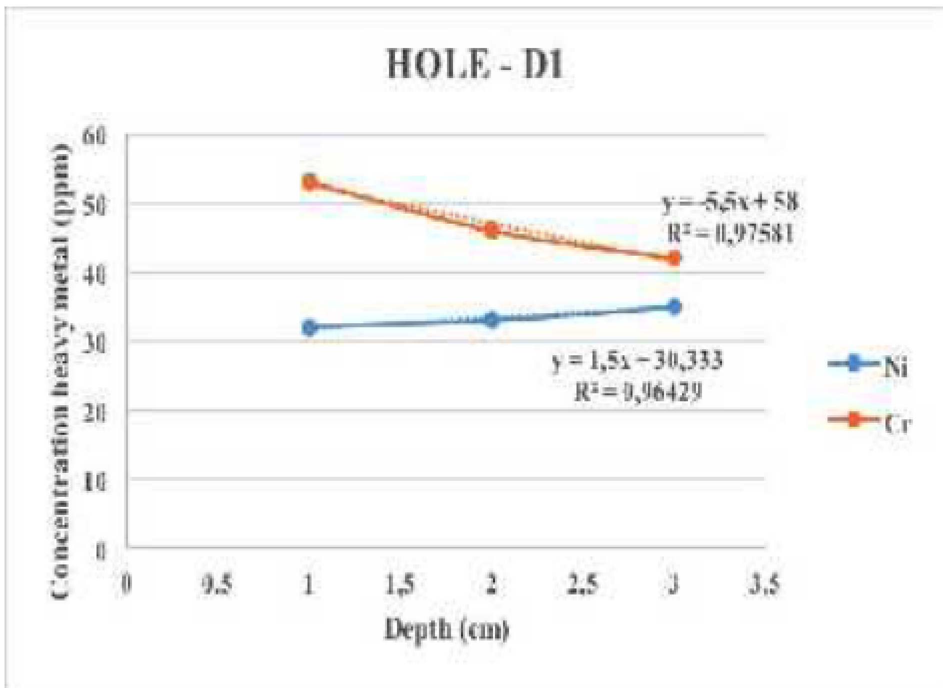

Figure 5. Graph of the analysis result of Ni and Cr heavy metal for Hole D1 at a depth of 0 to 10 cm, 10 to 20 cm, and 20 to 30 cm, on Antang Landfill, Makassar City, South Sulawesi Province, Indonesia.

The concentration of Ni metal on Hole D1 at a depth of 0 to 10 cm show a value of 32 ppm, whereas the concentration of Ni at a depth of 10 to 20 cm and 20 to 30 cm has increased in the range of 33 ppm and 35 ppm. The highest concentration of Cr metal on Hole D1 is found at a depth of 0-10 cm with a value of 53 ppm, while the concentration of Cr metal at a depth of 10 to 20 cm and 20 to 30 cm shows the values decreases exponentially to 46 ppm and 42 ppm.

The variation of pH value in the Antang Landfill for Hole A1 range from 5.00 to 6.00, Hole B1 range from 4.82 to 5.00, Hole C1 has the same value for each sample (4.83) and Hole D1 vary from 4.83 to 5.00. Detail values of pH are shown in table 1.

3.2. Discussions.

The sites of Antang Landfill at the holes of A1, B1, C1, and D1containing heavy metals of Ni and Cr exceeding the threshold value (table 1). The results showed that the total concentration of Ni and Cr heavy metals in Antang Landfill was spread horizontally with a highly variable amount at each depth on the soil surface (topsoil), except Cr heavy metal at a depth of 10 to 20 cm and 20 to 30 cm which is the values are below from threshold values (10 ppm). This area is still in normal limit according to the Government of Republik Indonesia [20]. The average of pH for Hole A1 and D1 ranging from 4.83 to 6, whereas pH in Hole B1 and C1 averaged about 4.82 to 5 and acidic.

Nickel (Ni) in the soil is widely accumulated in Horizon-B as a mixture of oxides or humus or organic matter [21]. Most of Ni in the soil is Ni $^{2+}$, whose solubility increases in low pH. Metal Ni most often settles as Nickel Ferrite ($NiFe_2O_4$) according to the research [22], while waste contains a lot of Ni, the use of it as fertilizer causes Nickel accumulation above the soil surface (Top Soil) according to these [22]. Nickel is an anthropogenic source such as fuel combustion. The average content of chromium (Cr) in the Earth's crust is 125 mg/kg. Some typical minerals containing Cr are chromite ($FeCr_2O_4$) and Crocoite ($PbCrO_4$). Chromium is very important for some organisms, Cr^{3+} is considered harmless, while Cr^{6+} is highly toxic. Some compounds are known to be carcinogenic, Cr^{6+}

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is more mobile than Cr . Increased Cr concentration on Antang Landfill soil caused by human activity, weathering, Cu fusion, natural gas burning, waste spray, and waste incineration.

The increasing of heavy metal content in the soil around the Antang Landfill shows that metal has been concentrated in the ground. As the soil was contaminated for a long time, the heavy metal content continues to increase, makes existing organic compounds to be degraded. Therefore, the heavy metal content in the soil is increasing. In Table 1, it can be seen that the concentrations of Ni and Cr metals on topsoil (decomposed waste) are still high accumulated. In the case of high and continuous rainfall, it can result in seepage downwards [23]. At Antang Landfill site there are many digging wells and houses [14]. The existence of Antang Landfill, in addition to water seepage that empties into the river, will affect the environmental quality around the landfill.

The increasing of heavy metal of Ni and Cr on the soil surface (topsoil) around Antang Landfill is still high accumulated. This is due to anthropogenic or human activity, Leachate and soil characteristics which are supported by a very acidic pH. In case there is very high rainfall, it can continue to permeation to the bottom, while seepage will disembogue into the river [24-27]. The heavy metal will be carried by Leachate, settled in the ground, and accumulated in the soil [28]. The density will affect soil dan water environmental quality around the landfill. Meanwhile, the good quality is very important for those around Antang Landfill, as most people are still using digging wells as drinking water [14].

The total heavy metal in soil is highly dependent on the clay content, in which 96% of Ni is found in the clay fraction [29], while the amount of Ni and Cr metal contamination is modified by soil pH. Ni tend to have high mobility under acidic conditions, as well as to the formation of soluble metal sulfides with very low mobility under reduced metal conditions in soils which can be enriched depending on the dominant factors present in the weathering environment, depending on local geology, the metal concentration of soils may exceed the general range (table 1).

The landfill is one main source of metal increased levels in the soil environment. Migration of contaminants from a landfill to the ecosystem is a complex process. Antang Landfill in Makassar City is categorized as Ultisol soil (a reddish soil containing a lot of clay), thus showing plasticity, triggering flooding and surface water pollution [15]. The color of the soil is due to the metal content, especially the oxidized iron and aluminum (weathered soil). The average analyzed soil pH at Antang Landfill ranged from 4.82 to 6, with an average value of 4.84 and average temperature ranging from 5°C to 31°C (table 1). pH plays an important role in metal bioavailability and soil toxicity to surrounding areas [30, 31].

The pH may affect metal mobility in the soil [7, 15]. Low of acid pH will help the availability of micronutrients, mobility, and redistribution of heavy metals such as Cu, Pb, Zn, Cr, Cd, Ni and Hg in various fractions due to increased solubility of ions in acidic soil environments, resulting in heavy metal concentrations increase inside soil [7, 32]. If the soil solution is too acidic, the plant cannot take advantage of N, P, K and other nutrients they need. In acid soil (low pH) the soil is dominated by Al, Fe and Mn ions.

These ions will bind nutrients needed by plants, especially elements P, K, S, Mg. So the plants cannot absorb food well despite a lot of nutrient content in the soil. In acid soil, any micro-content such as high Ni and Cr may poison the plants [32, 33]. Those heavy metals are very harmful to the health of the population, especially those living in the vicinity of the landfill, as they can cause cancer and lung damage, children's IQ or intelligence level decrease. The disease is a threat to humans that can cause death [32, 34, 5, 11, 35, 36].

4. Conclusion

The results of this study show that heavy metals contaminate the soil around of Antang Landfill, Makassar City, for Hole A1, B1, C1, and D1 Ni and Cr with exceeding-limit concentration in every depth, except Cr metal in Hole B1 with the depth of 10 to 20 cm and 20 to 30 cm (10 ppm), which is still on the average threshold value. pH of the soil is acidic and is one of the main factors affecting the mobility/solubility of metals in the soil environment. Under this pH condition, soil potentially resists

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further additional heavy metal loads. These heavy metals tend to enlarge bio and induce long-term adverse effects on ecosystems regarding toxicology to humans.

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