Distribution of Manganese Heavy Metal (Mn) in Soil Around of Antang Landfill, Makassar City, Indonesia

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Abstract. The Study has been conducted on the distribution of heavy metal content of manganese (Mn) on landfill in Antang, Makassar. The study aims to determine the presence of heavy manganese metal (Mn) in the landfill of Antang Makassar. There are 4 lines namely line A sampling points (A1, A2 and A3), line B sampling points (B1, B2 and B3), line C sampling points (C1, C2 and C3) and line D sampling points (D1, D2 and D3) with a depth of (0-10, 10-20 and 20-30) cm. Total samples analyzed by heavy metal elements using ICP-OES method were 36 samples. The concentration of heavy metal manganese (Mn) in Antang landfill soil has spread horizontally. The results of the analysis showed the presence of heavy metal content of manganese (Mn) in the soil of Antang landfill, where the samples with the highest heavy metal content were found in line A sampling points (A1, A2 and A3) each depth (0-10, 10-20, 20-30) cm. Line C sampling point of C3 at the depth of (0-10 and 10-20) cm, i.e. sequentially (1660 and 1710) ppm. Line D (D1, D2 and D3 sampling points), except, at the sampling point D1 at a depth of 20-30 cm which is 1460 ppm is still below the normal limit, which is allowed by the Government of the Republic of Indonesia and the General of Drug and Food Control as a pollutant inside soil. Soil pH varies from 4.82 to 6 and is acidic. Soil pH significantly affects the solubility and mobility of metals, because most metals dissolve in acidic soils. The level of pollution of heavy metal manganese (Mn) for line A, line C and line D at the sampling points (A1, A2 and A3) at depths (0-10, 10-20 and 20-30) cm are included in the category of heavily polluted because the concentration of heavy metals Mn contained in the soil far exceeds a predetermined threshold. So that necessary remediation of appropriate prevention to prevent risks to humans and the environment.

1. Introduction

Makassar City experiences rapid development affecting the increase of waste production. Waste becomes serious issue along with the increased population in Makassar City. Waste landfill for the community of Makassar is an essential need to create comfortable environment in big cities. In one day, if the waste in Makassar City is not moved into the landfill, then the city is full with waste so that it will disturb the community’s comfort. The fact that cannot be avoided is that the recent landfill condition in several big cities does not meet the criteria as safe landfill for the environment. Waste becomes big issue in every country. The increase of population causes increase of community’s activities which means that there is also an increase of waste. Increase of waste will decrease the space and disturb the human’s activities so that it decreases the human’s life quality due to the waste issue. Therefore, right and good waste management system is required [1].
Several landfills have been closed since its location is near residence and the gas of air pollution from the waste decomposition is considered to be very disturbing for the community. According to [2], uncontrolled landfill is very dangerous for health and can damage the environment. Landfill can cause smell pollution which really affects the community living around the landfill in 2 km radius. Smell pollution from landfill is one of the pollutant components affecting the human’s life environment, whether it is in level of social, national, and comfort. Therefore, it is recommended that the government has the authority to take right action to overcome the smell pollution caused by landfill [3].

Landfill generally use open dumping method. Waste which is dumped and left open daily with the soil, and the waste and waste water collection which is not optimal can affect the groundwater quality around the landfill [4]. If the landfill does not have correct management, according to [5], it will produce solid waste. It contains dangerous toxic compound such as heavy metal and persistent organic pollutant (POPs), so that it creates pollution in the environment.

Tamangapa Antang landfill located in Bangkala Sub-District of Manggala is the main landfill for all areas in Makassar. It has been used since 1995 until now with the area width of 18.8 Ha. Tamangapa Landfill was prepared to contain need of 10 years. In fact, the landfill is still used until now, so that it is considered not able to contain any waste from Makassar anymore which reached 800 ton or around 4,000 cubic per day. Based on the record of Sanitary and Environmental Department of Makassar with the total population of 1.3 million people, there is around 3,800 m$^3$ urban waste produced each day. Meanwhile, maximum capacity of Tamangapa landfill is only around 2,800 m$^3$ urban waste for each day, so that additional landfill area is needed to dump 1,000 m$^3$ of remaining waste, of which 87% of the waste is organic, while the rest is inorganic including plastic and paper [6].

This research is due to the high pressure received by the soil due to the waste dump produced by domestic activities. Such pressure contaminates the soil. When a hazardous or toxic substance contaminates the soil surface, then it will evaporate, swept by rainwater and or enter the soil to sediment as toxic chemical substance in the soil. The toxic substance will directly affect human when they touch the soil or it can contaminate the groundwater and the air above it [7]. Around the soil of Makassar Antang landfill contains heavy metals Pb, Zn, Cu, Ni, Cu and Hg, far exceeding the threshold both laterally and vertically [8-10].

This research aimed to analysis the distribution of Manganese (Mn) heavy metal on the soil around Antang landfill. The research focuses on how the effect caused by the distribution of heavy metals on the soil around Tamangapa Antang landfill of Makassar towards the life of community around the landfill, in point 0 m, 5 m, and 10 m with the depth of 0-10 cm, 10-20 cm, and 20-30 cm.

2. Methods

2.1. Research Location

The research location administratively belongs to Bangkala Sub-Village, Manggala Sub-District, Makassar Municipality, of South Sulawesi Province. Geographically, this region is located in coordinate point of 119°, 29'–119°, 29', 40" East Longitude and 5°, 10'–5°, 10’, 40” South Latitude. The research location can be seen in figure 1.
Figure 1. Location Map and Sampling lines, for line A, line B, line C and line D, with depths of 0 to 10 cm, 10 to 20 cm and 20 to 30 cm (vertically and laterally) around the Landfill of Antang, Makassar.

2.2. Soil Sampling

2.2.1. Tools and Materials. Materials used included soil sample from Antang landfill of Makassar. For the sake of soil analysis need, a certain amount of chemical material in laboratory is needed, including: aquadest, HNO₃, HCl, H₂SO₄, HClO₄. The field tools used were hoes, shovel, crowbar, test well, hammer, plastic bag, label, GPS, and stationary. The analysis tools used in the laboratory included: Erlenmeyer 250 mld, drop pipette, petri dish, test tube, scale, stainless steel filter (2 mm), incubator, measuring cup of 100 mL, autoclave, rotary mixer, centrifuge of 18,000 rpm, shaker, ose needle, digital camera, mask, Bunsen, ice box, microscope, craft plastic, aluminum foil, preparation glass, object glass, filter paper (Whatman No. 42) which is in accordance with ASTM standard.

2.2.2. Soil Sample. Sample used in this research is the topsoil collected in Antang landfill area of Makassar. The soil sampling point determination was done by divided 4 points, which were line A, line B, line C and line D, in the depth of 0-10 cm, 10-20 cm, and 20-30 cm laterally.

2.2.3. Soil Sample Test. Before being tested, the soil was put into oven for 48 hours at 106°C [11-13], in order to ease the filtering process so that the particle does not stick to each other. Then it was destructed using wood hammer or ceramic hammer [11], sieved using stainless steel filter of 2 mm [14,15], saved in desiccator before being analyzed [13]. The soil samples that has been repaired was then brought into laboratory to be analyzed.

2.2.4. The Work Principle ICP-OES. The sample was weighed as much as 1 gram and put into crush porcelain and added by 2 Gram of Na₂CO₃ evenly, and put into oven at 800°C for two hours. After that, the samples that have been destructed, was added by aqua regia and left for ±12 hours. It was then moved into chemical glass and heated until it was almost dry. Then, the samples that have been dissolved were added by aquabidest as much as those that has been filtered. The resulted filtrate was put into mL and pressed by aquabidest until it reached the limit mark using ICP-OES.
3. Result and Discussion

3.1. Result

The analysis result of Manganese (Mn) heavy metal concentration using ICP-OES method for Line A, Line B, Line C and Line D at the depth of 0-10 cm, 10-20 cm and 20-30 cm, as much as 37 samples can be seen in Table 1. Meanwhile, the lateral analysis result of Manganese (Mn) heavy metal for Line A, sampling point (A1, A2 and A3) at the depth of 0-10 cm, 10-20 cm and 20-30 cm, in soil around Antang landfill of Makassar is presented in Figure 2.

Table 1. Analysis Result of Manganese (Mn) heavy metals concentration for line A, line B, line C and line D laterally at the depth of (0-10, 10-20 and 20-30) in the soil around Antang landfill of Makassar.

| Line | Hole | Depth (cm) | Concentration heavy metal (ppm) Mn | pH | Temperatur e °C |
|------|------|-----------|----------------------------------|-----|-----------------|
| A    | A1   | 0-10      | 3430                             | 6   | 26              |
|      |      | 10-20     | 3280                             | 5   |                 |
|      |      | 20-30     | 3090                             | 6   |                 |
|      | A2   | 0-10      | 3480                             | 6   |                 |
|      |      | 10-20     | 3330                             | 5   | 25              |
|      |      | 20-30     | 2740                             | 6   |                 |
|      | A3   | 0-10      | 3140                             | 5   |                 |
|      |      | 10-20     | 2920                             | 5   | 25              |
|      |      | 20-30     | 2530                             | 6   |                 |
|      | B1   | 0-10      | 129                              | 5   |                 |
|      |      | 10-20     | 95                               | 4.78| 30              |
|      |      | 20-30     | 93                               | 4.82|                 |
|      | B2   | 0-10      | 509                              | 5   |                 |
|      |      | 10-20     | 622                              | 4.82| 28              |
|      |      | 20-30     | 407                              | 4.82|                 |
|      | B3   | 0-10      | 321                              | 5   |                 |
|      |      | 10-20     | 719                              | 4.82| 26              |
|      |      | 20-30     | 598                              | 4.84|                 |
|      |      | 0-10      | 212                              | 4.82|                 |
|      | C1   | 0-10      | 104                              | 4.83| 31              |
|      |      | 10-20     | 104                              | 4.83|                 |
|      |      | 20-30     | 121                              | 4.84|                 |
|      | C2   | 0-10      | 1400                             | 4.83|                 |
|      |      | 10-20     | 1450                             | 4.83| 27              |
|      |      | 20-30     | 1010                             | 4.83|                 |
|      |      | 0-10      | 1660                             | 4.83|                 |
|      | C3   | 0-10      | 1710                             | 5   | 26              |
|      |      | 10-20     | 1710                             | 5   |                 |
|      |      | 20-30     | 1080                             | 5   |                 |
|      |      | 0-10      | 1570                             | 4.83|                 |
|      | D1   | 0-10      | 1500                             | 4.84| 26              |
|      |      | 10-20     | 1460                             | 5   |                 |
|      |      | 20-30     | 1460                             | 5   |                 |
|      |      | 0-10      | 2230                             | 4.83|                 |
|      | D2   | 0-10      | 2330                             | 4.85| 26              |
|      |      | 10-20     | 2330                             | 4.85|                 |
|      |      | 20-30     | 698                              | 5   |                 |
|      |      | 0-10      | 2000                             | 4.84|                 |
|      | D3   | 0-10      | 1929                             | 5   | 27              |
|      |      | 10-20     | 1929                             | 5   |                 |
|      |      | 20-30     | 1600                             | 4.85|                 |
Figure 2. Graph of lateral analysis result of Manganese (Mn) heavy metals for line A and sampling points (A1, A2 and A3) at the depth of 0-10 cm, 10-20 cm and 20-30 cm, in the soil around Antang landfill of Makassar.

Line A showed that Mn heavy metal concentration at the depth of 0-10 cm of A1 sampling point was around 3,430 ppm, A2 sampling point obtained concentration of around 3,480 ppm, and A3 sampling point obtained concentration of around 3,140 ppm, showing that irregular concentration from the deepest point to the outermost point (A1, A2 and A3) has exceeded the normal limit. At the depth of 10-20 cm, A1 sampling point obtained concentration of 3,280 ppm, A2 sampling point obtained concentration of around 3,330 ppm, while A3 sampling point obtained concentration of around 2,920 ppm, showing irregular concentration from the deepest point to the outermost point (A1, A2 and A3) which has exceeded the normal limit. At the depth of 20-30 cm, A1 sampling point obtained concentration of around 3,090 ppm, A2 sampling point obtained concentration of around 2,740 ppm, while A3 sampling point obtained concentration of around 2,530 ppm, showing that the concentration decreased from the deepest point to the outermost point (A1, A2 and A3), which has exceeded the normal limit.

The lateral analysis result of cobalt (Co) heavy metal for line B, sampling points (B1, B2 and B3) at the depth of 0-10 cm, 10-20 cm and 20-30 cm, in the soil around Antang landfill of Makassar can be seen in figure 3.

Figure 3. Graph of lateral analysis result of Manganese (Mn) heavy metals for line B, sampling point (B1, B2 and B3) at the depth of 0-10 cm, 10-20 cm and 20-30 cm, in the soil around Antang Landfill, Makassar.

Line B showed that the concentration of Mn heavy metal for sampling point of B1 at the depth of
0-10 cm obtained was around 129 ppm, sampling point of B2 obtained concentration of around 509 ppm, sampling point of B3 obtained concentration of around 321 ppm, showing irregular concentration from the deepest point to the outermost point (A1, A2 and A3) which were still below normal. At the depth of 10-20 cm, the sampling point of B1 obtained concentration of around 95 ppm, sampling point of B2 obtained concentration of around 662 ppm, while B3 sampling point obtained concentration of around 719 ppm, showing that the concentration increased from the deepest point to the outermost point (B1, B2 and B3), which were still below normal limit. At the depth of 20-30 cm, B1 sampling point obtained concentration of around 93 ppm, B2 sampling point of around 407 ppm, B3 sampling point of around 719 ppm, showing that the concentration increases from the deepest point to the outermost point (B1, B2 and B3), and were still below limit.

The lateral analysis result of Cobalt (Co) heavy metal for line C, sampling points (C1, C2 and C3) at the depth of 0-10 cm, 10-20 cm and 20-30 cm, in the soil around Antang Landfill, Makassar is presented in figure 4.

Figure 4. Graph of lateral analysis program of Manganese heavy metal for Line C, sampling points (C1, C2 and C3) at the depth of 0-10 cm, 10-20 cm and 20-30 cm, in soil around Antang Landfill, Makassar.

Line C showed that Co heavy metal concentration for C1 sampling point at the depth of 0-10 cm obtained concentration of around 212 ppm, C2 sampling point obtained concentration of around 1,400 ppm, C3 sampling point obtained concentration of around 1,660 ppm, showing that the concentration increases from the deepest point to the outermost point (C1, C2 and C3), which were still below normal, except C3 sampling point which has exceeded the normal limit. At the depth of 10-20 cm, C1 sampling point obtained concentration of around 104 ppm, C2 sampling point obtained concentration of around 1,450 ppm, C3 sampling point obtained concentration of around 1,710 ppm, showing that the concentration increased from the deepest point to the outermost point (C1, C2 and C3), which were still below the normal limit, except C3 point sampling which has exceeded the normal limit. At the depth of 20-30 cm, C1 sampling point C1 obtained concentration of around 121 ppm, C2 sampling point obtained concentration of around 1,010 ppm, while C3 sampling point obtained concentration of around 1,710, showing that the concentration increased from the deepest point to the outermost point (C1, C2 and C3), which were still below the normal limit except C3 sampling point which has exceeded the normal limit.

The lateral analysis result of heavy metal concentration for Line D at the depth of 0-10 cm, 10-20 cm and 20-30 cm in the soil of Antang landfill of Makassar is presented in figure 5.
Figure 5. Graph of lateral analysis result of Manganese (Mn) heavy metal for Line D, sampling points (D1, D2 and D3) at the depth of 0-10 cm, 10-20 cm and 20-30 cm, in the soil around Antang Landfill, Makassar.

Line D showed that of Mn heavy metal for D1 sampling point at the depth of 0-10 cm obtained concentration around 1,570 ppm, D2 sampling point obtained concentration of around 2,230 ppm, D3 sampling point obtained concentration of around 2,000 ppm, showing irregular concentration from the deepest point to the outermost point (D1, D2 and D3) which has exceeded the normal limit. At the depth of 10-20 cm, D1 sampling point obtained concentration of 1,500 ppm, D2 sampling point obtained concentration of 2,330 ppm, D3 sampling point obtained concentration of 1,929 ppm, showing irregular concentration from the deepest point to the outermost point (D1, D2, and D3), which have exceeded the normal point, except D1 sampling point which was still in the normal limit. At the depth of 20-30 cm, D1 sampling point obtained concentration of around 1,460 ppm, D2 sampling point obtained concentration of around 698 ppm, D3 sampling point obtained concentration of around 1,600 ppm, showing irregular concentration from the deepest point to the outermost point (D1, D2 and D3), which have exceeded the normal limit, except S2 and D3 sampling points which were still below normal limit.

3.2. Discussion
The four locations of Antang landfill of Makassar City, South Sulawesi, Indonesia, which are point A, point B, point C, and point D contained Manganese (Mn) heavy metal. Manganese (Mn) heavy metal concentration in Antang landfill has spreaded laterally on the top soil. The analysis result showed that the total of Manganese (Mn) heavy metal concentration in Antang landfill has spreaded laterally with various concentration in every point and depth in soil environment (Table 1). The normal limit of heavy metal concentration allowed by the Government of the Republic of Indonesia and General of Drug and Food Control [16], as contaminant in soil for Manganese (Mn) heavy metal is 1,500 ppm.

The addition of waste containing Manganese (Mn) heavy metal mixed with organic material can increase the heavy metal potential on the topsoil. Observation result found that waste which is dumped at Antang landfill contained high organic material, because most of them were from household. In addition several parts of waste were identified from battery or accu water material, used cans, paint, mining activity, metal production, wood production, phosphate fertilizer production, forest burning, and other which were expected to contain Manganese heavy metal. Waste which contains much Manganese (Mn) heavy metal mixed by organic material can increase heavy metal potential on the topsoil [17,18].

The high content of Manganese (Mn) heavy metal around Antang landfill of Makassar showed that Manganese (Mn) heavy metal has concentrated in the soil. Manganese (Mn) heavy metal content in the soil is caused by soil which is contaminated for quite long time and the heavy metal content adds continuously, so that the existing organic compound experiences degradation. Therefore, Manganese
(Mn) heavy metal content in the soil around Antang landfill of Makassar in line A, line B, and line C increased.

Soil which is relatively acid has increased micronutrient solubility and mobility, so that the heavy metal concentration in the soil increases. If the soil is too acid, the plant cannot utilize N, P, K, and others nutrient they need. Acidic soil is dominated by Al, Fe and Mn ions. These ions can bind the nutrient which is needed by the plant, especially the elements of P, K, S, Mg so that the plant cannot absorb the food well, although there is a lot nutrient content in the soil. In the acidic soil, micro Mn content is high so that it poisons the plant.

Total heavy metal in the soil is based on the content, in which manganese heavy metal content has low mobility at pH<7 so that its existence in the soil can increase. The increase of manganese (Mn) heavy metal mobility in point A, point B, point C, and point D, is caused by acidic soil pH. The occurrence of increased soil reduction is caused by organic material addition as well as the increase of organic acids produced by organic material.

The four locations of Antang landfill of Makassar, which are line A, line B, line C, and line D contained Manganese (Mn) heavy metals which has exceeded the normal limit. It is mostly because line A, line B, line C, and line D still actively received waste and close to the road. The decomposition of waste was till in process. There were many wastes dumped at the landfill without being sorting. Several inorganic wastes were still in decomposition process on the topsoil. The soil’s pH in Antang landfill Makassar was analyzed at the range of 4.82 to 6, the mean temperature was between 25°C-31°C [18]. pH has essential role in bioavailability of heavy metals and soil toxicity to the area around it. pH affects the metal mobility in the soil [11,15]. Acidic pH will help the availability, mobility, and redistribution of Manganese (Mn) heavy metal in various fraction since there is increase in Mn$^{2+}$ ion solubility in acidic soil environment [11].

According to Mengel and Kirkby [20], Mn content in the soil is generally at the range between 200 and 3,000 ppm. In the soil, Manganese is at least in the main form, which is Mn divalent ion bond with clay mineral and organic material as well as tetravalent ion in the form of oxide and sometime it associates with ferry-oxide connection. Research result [21], found that the absorption of Mn metal element is varied according to the plant species and its absorption level is generally lower than other divalent ion including calcium and Magnesium.

The most important manganese form in the soil is Mn$^{2+}$ ion and Mn oxide existed in the forms of trivalent and tetravalent. Mn in divalent form can be fixated by clay mineral and organic material, and such Mn ion is way more important compared to Mn ion in the soil, since the fixated ion in complex can be in balance form with the ion absorbed by plant, so that the factors of excessive and toxicity of Manganese can be decreased [21,22].

Manganese (Mn) heavy metal belongs to essential mineral nutrient needed in relatively small amount. Plant which experiences lack of Mn shows black spots and then develops chlorosis symptom between bones and leaves [21]. The presence of Mn$^{2+}$ heavy metal ion in the soil as micro nutrient element in a certain concentration is needed for plant fertility [23]. Plant needs micro elements less than 0.01% or 100 ppm. Those elements are needed by plant only in very low concentration and often toxic at higher concentration [24]. Excessive amount of micro element in soil triggers the incidence of toxication, especially in plant. Meanwhile, in critical condition, it causes inhibited plant growth.

4. Conclusion

Distribution of Manganese (Mn) heavy metal concentration has spreaded in the topsoil laterally. The analysis result showed that the concentration of Manganese (Mn) heavy metal in line A, line B, line C and line D in every depth has exceeded the normal limit, except line B at the depth of 0-10 cm, 10-20 cm and 20-30 cm of B1, B2 and B3 sampling points, line C of C2 and C3 sampling points at the depth of 0-10 cm and 10-20 cm, Line D of D1 and D2 sampling points at the depth of 0-10 cm and 10-20 cm, of which the concentration was still above normal limit allowed by the Government of the Republic of Indonesia and general of Drug and Food Control. Manganese (Mn) heavy metal content in four locations of Antang landfill of Makassar was still accumulated highly. The excessive amount of micro
element including Manganese (Mn) heavy metal in the soil triggers the incidence of toxicity, especially in the soil, while in critical condition, it causes inhibited plant growth.

Acknowledgement

We would like to thanks to Mining Engineering Department, Moslem University of Indonesia for all the facilities provided during our research. The Authors also thank to editor and anonymous reviewers for their reviews and comments on the manuscript.

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