Assessment of Heavy Metals in Municipal Solid Waste Dumpsite in Harar City, Harari Regional State, Ethiopia

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Abstract: This study was conducted on municipal solid waste dumping sites at Selate and Kile in Harar City, Harari Regional State, Ethiopia, to investigate concentration of heavy metals in soil. Three soil sampling points were purposively selected for fresh, intermediate and old wastes dumping areas. A composite soil samples were also collected from control areas near the dumping sites where wastes were not dumped separately with similar depths with from dumping sites. Results showed that the mean concentrations of these metals in the domestic municipal solid waste were higher in decreasing order of Zn>Mn>Cu>F>Pb>Co>Cd>Ni>Cd>Ni>Cr at Selate and Kile dumping sites, respectively. The pH values ranged from 8.1-8.1 and 7.7-8.1 for soil from decomposed and intermediate dumping respectively at Selate municipal solid waste dumping site. It was also slightly similar at Kile site. Concentrations of heavy metals were higher in soils from decomposed and intermediate waste dumping areas at 0-20 cm and 20-40 cm depth compare to control sites. At both dumping sites concentration of heavy metals were below the acceptable levels of deferent standards. The statistic correlation analysis indicated that pH of the soil had close relationship with most of heavy metals. Even though the concentrations of heavy metals were below the acceptable levels of different standards, rule and regulation of waste treatment system and recycling of waste should be applied for sustainable use of resources and environmental quality.

Keywords: Selate, Kile, Heavy Metals, Municipal Solid Waste, Dumping Sites

I. INTRODUCTION

The disposal of domestic, commercial and industrial garbage in the world is a problem that continues to grow with human civilization [1]. Solid municipal wastes, due to insufficient collection and improper disposal, is a major concern for many rapidly growing cities in developing countries [3]. Lack of appropriate planning, resource constraint and ineffective management of domestic and industrial solid wastes are also among the factors aggravating the problems associated with municipal solid wastes. So far, no methods of municipal wastes disposal that is completely safe [2]. Amongst all the classes, solid municipal waste pose the greatest threat to life since it has the potential of polluting the terrestrial, aquatic and aerial environment. Solid municipal wastes are sources of environmental pollution through introduction of chemical substances above the threshold limit of the environment [50]. Land pollution by component of refuse such as heavy metals has been of great concern in the last decades because of their health hazards to man and other organisms when accumulated within a biological system [5]. Recent studies have also shown that waste dumpsites can transfer significant levels of these toxic and persistent metals into the soil environment. Eventually, these metals can be taken up by plant and enter into the food chain [61, 52, 32]. Plant uptake of heavy metals would be high from soils with higher concentration of such metals. However, uptake of heavy metals by crop plants could be influenced by factors such as metal species, plants species and growth stage [61]. Therefore, to alleviate
environmental problems due to municipal waste disposal, establishment of appropriate disposal sites and management are paramount important. Open dumping sites of solid wastes are very common in developing countries [56]. Most of Ethiopian cities currently depend on open dumping sites for solid waste disposal. In open dumping sites, solid wastes are generally spread over large areas which are sources of food and harborage for rats, flies and vermin, and also be a source of bad odor and smoke nuisance, a fire hazard, and a cause of water pollution [56]. In general, open dumping sites for solid wastes are unsatisfactory for health, environmental and aesthetic grounds.

Harar city municipal landfill locations are non-engineered low lying open dump. The landfill site is not equipped with any leachate collectors. Therefore, all the leachates generated find paths in to the surrounding environment. These leachates generally may contain large amounts of organic matter (biodegradable, but also refractory to biodegradation), as well as ammonia-nitrogen, heavy metals (e.g. copper, iron, zinc, lead, manganese etc.), chlorinated organic and inorganic salts (e.g. chloride, sulfate, sodium etc.), which are a great threat to the surrounding soil, groundwater and even surface water [53, 54]. Selate and Kille, the districts in Harar city, collected wastes have been used as fertile soils for the cultivation of some fruits and vegetables. Some farmers collect the decomposed parts of the dumpsites and apply to their farms as manure without sufficient information on the chemical composition of the decomposed waste. The cultivated crops may take up heavy metals either as mobile ion in the soil solution or the presence of the heavy metals may hinder the uptake of other nutrients by the crops. Therefore, characterization of Heavy metals in the solid wastes and in soils at the dumping sites could indicate environmental pollution potential of municipal solid wastes. To provide scientific information to government organization like municipal bureaus about the environmental hazards of municipal solid wastes, assessment of heavy metal contents of the solid waste is vital. The generated data can serve as baseline for designing and implementing a better municipal solid waste management options that could be acceptable management strategy undoubtedly, create healthy to the community. Hence, this study intended to investigate the concentration levels of some selected heavy metals in municipal solid waste and soil at waste dumpsite in municipal area of Harar city.

II. MATERIAL AND METHODS

A. Study Location

The study was conducted in Harari Regional State, located in the eastern part of Ethiopia (Figure 1). Total area of the region is about 343.21 km². Geographically, the region is located between 42.03° – 42.16° north of latitude and 9.11° - 9.24° east of longitude. The region shares common boundaries with woredas of East Harerghe Zone of Oromia Regional State. Administratively; Harari Regional State is divided in six urban and three rural administrative woredas (main kebeles). These administrative kebeles are further divided into 19 sub-kebeles (in urban) and 17 sub-kebeles (in rural). The region is mainly categorized into two agro-ecological zones. 90% of the land area of the region is estimated to be mid-high land (weynadega), the altitude range 1400 – 2200 meter above sea level, while the remaining 10% is kola (approximately found below 1500 masl). The city of Harar is the capital of Harari Regional State; which is located in east at a distance of 525 Km from Addis Ababa. The elevation above sea level of the city ranges from 1600 to 1900 meter.

Figure1. Map of Study Area
B. Sampling Technique for Solid Wastes and Soils
To determine the concentration of heavy metals from municipal solid waste and soil at two dumping sites were selected from Harar municipal solid waste dumping site, Kile dumping site 11 km from Harar city on -side of the road to Bible and the second dumping site is 2 km far from Gugol Selate site. Both solid waste dumping sites are open with non-engineered lower lying. There is no any leachate collection and treatment system at both sites. Therefore, the generated leachates find paths into the surrounding environment.

To assess heavy metals concentration in the decomposed municipal solid waste, from both dumping sites. Six decomposed municipal solid waste dumping points were selected purposively for each dumping sites to form two composite decomposed municipal solid waste samples separately. Decomposed municipal solid waste samples (DMSW) were collected from dumping points that have been used by farmers as manure. Non degradable materials were separated from the decomposed waste manually. The collected samples were air-dried, packaged in polythene bags and taken to laboratory for preparation.

To assess concentration of heavy metals in soil at both dumping sites, 3 soil sampling points were purposively selected for fresh, intermediate and decomposed wastes were dumped. The wastes were removed from the surface and soil samples were collected from 0-20, and 20-40 cm depth using auger. A total of 6×2 = 12 soil samples were collected for both dumping sites separately. Two composite soil samples were made from samples collected from each sampling point with respective depth for each dumping sites separately. A composite of control samples for each dumping site with similar depths to dumping sites were taken from 100 m away from dumping sites. The samples were packed in plastic bags and taken to laboratory.

The wet soils and solid waste sample were air dried. Samples were mixed frequently to expose fresh surface to dryness. The samples were grind after drying and sieved through a 2 mm sieve, coarse particles greater than 2 mm size was discarded. The ground samples were stored for digestion and subsequent analyses.

C. Analytical Procedure
The pH was measured by pH meter in suspension of 1:1 ratio of soil and water mixture. 10 g of air dried soil and DMSW (< 2 mm) was weighed and transferred into 100 mL beaker and 10 mL of distilled water was added. The mixture was stirred by a magnetic stirrer and the pH was measured after allowing the suspension to stand for 1 hr at room temperature [58].

For determination of electrical conductivity 10 g DMSW and soil were weighed and transfer into 100 mL beaker and 50 mL of Deionized water was added in it. Then, the mixture was stirred using an automatic stirrer for 30 minutes. Finally, the conductivity of each sample was measured from the upper part of the mixture after the suspension was settled (ICARDA).

The solid waste and soil samples were digested with concentrated nitric (HNO₃) and perchloric (HClO₄) acids. 3 mL of concentrated HNO₃ was added to 0.5 -1.0 g samples. The acid sample mixture was heated to about 145°C for 1 hour. After 1 hour heating, 4 mL concentrated HClO₄ was added and the mixture was heated to 240°C for further 1 hour. After complete digestion of all samples, the digest was allowed to cool to room temperature. The content of the digest was filtered through whatman No. 42 filter paper and diluted to 50-mL volume with deionized water. The diluted digest was taken for subsequent analysis of heavy metals as described by [22].

The environmentally hazard heavy metals extractions were replicated for accuracy and the concentrations of Fe, Mn, Cu, Zn, Cd, Ni, Pb, Co, and Cr were measured by atomic absorption spectrophotometer model number 210VGP. Concentration of each heavy metal were measured at specific wavelength; Chromium (357.9nm), Lead (217nm), Zinc (324.8nm), Iron (248.3nm), Cadmium (228.8nm).

D. Data Analysis
Data obtained were analyzed using statistical software for Microsoft Excel and using SPSS V20.0 for Windows, while the tables and figures were to present the mean values. The heavy metal concentrations at both dumping sites were compared using T test at p ≤ 0.05 for significant difference.

III. RESULTS AND DISCUSSION
A. pH, Electric Conductivity and Heavy Metals Concentrations in Municipal Solid Waste at Selate and Kile Dumping Sites
pH: Mean pH values of decomposed municipal solid wastes (DMSW) were alkaline (7.99 and 8.05) for Selate and Kile dumping sites, respectively (Table 1). Relatively, there is very small numerical difference in pH values of decomposed wastes at both dumping sites. pH range of 6.5 to 8.0 is acceptable for composting, and most common feed stocks fall within this range [59]. However, pH of decomposed waste at Kile dumping sites was slightly greater than the acceptable range suggested by [59]. The relatively very small
difference (0.06) in pH values of the decomposed wastes suggests that the wastes might be from same sources and types. Higher pH value of Kile (8.05) than Selate (7.99) dumping sites could be attributed to more concentration of heavy metals (Fe, Mn, Zn, Cu and Pb) (Table 1). Some of these metal ions have characters to form basic reactions [45]. The recorded pH for both sites was close to the similar finding by [38] at Matuail and Khulna MSW dumping sites 7.76 and 7.95, respectively, in Bangladesh.

Electrical conductivity: EC of the decomposed municipal solid wastes were 1.12 and 0.98 ms/cm at Selate and Kile dumping sites, receptively as shown in (Table 1). EC of the wastes at Selate is greater than that of Kile by 0.14 ms/cm while its pH is less by 0.06 than that of decomposed waste at Kile. This indicates the impact of pH on the solubility of soluble materials in the decomposed wastes.

Heavy metals concentrations in decomposed municipal solid waste: The concentrations of most heavy metals (Fe, Mn, Zn, and Cu) in decomposed municipal solid waste at Kile dumping site were relatively greater than at Selate dumping site (Table 1). More accumulation of metallic wastes was observed during waste samples collection at Kile site than at Selate site. Therefore, higher concentration of these metals at Kile dumping site might be due to more metallic wastes at Kile. The presences of Cr, Ni, and Co in decomposed wastes at both dumping sites were lower compared to other heavy metals. Their concentrations were less than 1mg/kg (Table 1). Concentration of Cd (1.14 mg/kg), Co (0.82 mg/kg), Zn (69.7 mg/kg) and Mn (31.29 mg/kg) were greater than the finding of similar study in Bangladesh [38], but concentration of Cu, Pb and Ni were low. This suggests that generation rate and waste types depend on country culture, feeding style and economic developments.

The main composition of municipal wastes are leather tanning, wood preserving, textiles, buttons, zips, coins, dental braces, orthodontic application (appliances used in the treatment of problems concerning the teeth and jaws) household appliances tools, artificial joints, jewelry, batteries, hair spray and magnetic tape [40]. The identified composition of wastes at Kile dumping sites during sampling was more metallic. Thus the differences in heavy metals concentration at both sites could be due to differences in quantity of these metals dumped with wastes. [39] reported that concentration of heavy metals in waste vary from time to time and site to site due to variables such as waste composition, moisture content, etc.

Table 1: pH, EC and heavy metals concentration of decomposed municipal solid waste

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<th>Sites</th>
<th>pH</th>
<th>EC (mS/m)</th>
<th>Heavy metal concentration (mg/kg)</th>
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<td>Fe</td>
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<tr>
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<tr>
<td>Kile</td>
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<td>0.982</td>
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[33], revealed variation in concentration of heavy metals such as Fe, Cu, Cd, Ni and Cr in decomposed solid waste and soil samples during the summer and monsoon seasons. In each case, higher concentration of heavy metal was noted during the dry season (summer) as compared to that observed during the wet season (monsoon); this study was conducted at rainy season which might be one year for low concentration of heavy metals in DMSW.

Generally, at both dumping sites the decomposed municipal solid wastes (DMSW) contain low metallic burden compared with EU and WHO standards [44]. Data in Table 1 show mean concentration of heavy metals in the DMSW follow the order of Zn > Mn > Cu > Fe > Pb > Co > Cd > Ni > Cr in Selate dumping site and Zn > Fe > Mn > Cu > Pb > Cd > Ni > Co > Cr in Kile dumping site. Thus, contamination levels at Selate dumpsite with Zn, Mn, Cu, Fe and Pb were at a higher level, whereas contamination with Zn, Fe, Mn, Cu, Pb and Cd were at a higher level at Kille dumping site. At both dumping sites concentration of zinc was higher than others heavy metals. High level of Zinc could be attributed to zinc containing organic waste, zinc batteries and fluorescent lamps. [15], also reported higher zinc concentration than other heavy concentrations in decomposed MSW.

[36], pointed out that lead (Pb), cadmium (Cd), copper (Cu) and nickel (Ni) are potentially toxic to plants and animals and have been shown to accumulate in the food chain. The same authors confirmed that zinc (Zn) is an essential micronutrient for plants, but at high concentrations it is phytotoxic and may reduce the productivity of the land. It is highly toxic to plants, animals, and humans. So, continuous dumping of wastes can disturb natural soil physical, chemical and biological characteristics, pollute ground water and causes hazardous impact on human health.

Application of these municipal solid wastes as organic fertilizer to soils may be major potential source of metal pollution into farm lands. [10], reported that food crops grown on soils contaminated with heavy metals absorb the metal ions depending on their metal uptake and storage capabilities. At Kille site, the wastes have been dumped on farmlands and, near avocado and mango plants.
Therefore, these heavy metals can easily enter into the food chain though soil to plant system. [10], revealed that soil to plant transfer is a major pathway of human exposure to toxic metals via the food chain. The transfer of metals from the compost of the MSW into the soil and subsequently into the vegetables could be expected. Therefore, excessive use of these municipal solid wastes as manure may be the pathway for transferring heavy metals to human beings and cause serious health problems.

The maximum concentration of lead in compost is 65, < 100, 70-1000, 300 and 150 mg/kg for Netherlands super clean compost, Netherlands “clean compost, EU-Range, USA standards and German Standards, respectively [44]. In decomposed MSW, maximum concentration of lead was 5.17 and the mean was 4.12 for both sites which were below the limit standards set by those organizations. But continuous accumulation of this heavy metal might contaminate soil and ground water. Cadmium concentration is 0.7, 1, 0.7-10, 39 and 3 mg/kg for Netherlands super clean compost, Netherlands “clean compost, EU-Range, USA standards and German Standards, respectively [44]. The maximum and mean values of Cd concentrations were 1.3 and 0.89 mg/kg, respectively, which are greater than Netherlands, super clean compost but for other standards below the accepted ranges.

Generally, the concentrations of heavy metals recorded in decomposed municipal solid wastes were below the limits but continuous use of these wastes as manure may be hazardous for plants and animal. The use of municipal solid waste and waste water contaminated with heavy metals for irrigation over long period of time increases the heavy metal contents of soils above the permissible limit. Ultimately, increasing the heavy metal content in soil also increases the uptake of heavy metals by plants depending upon the soil type, plant growth stages and plant species [7].

World have not the same standards for toxic metals. Each country has different standards. Even one country has two standards, like Netherlands super clean compost, Netherlands “clean compost. The differences are that principle of mass balance, i.e. the heavy metal load should not exceed the runoff and absorption in plants. In other countries, risk assessment has been the guide for determination of limits. Related to maximum loads per hectare and year are also regulations regarding soil compatibility [41]. In developed countries standards are created based on its amount or load of toxic waste generation rates. So, the industrialized countries standards may not be fit for developing country which generates none or low amount of toxic wastes.

B. pH, Electrical conductivity and Heavy metals Concentrations in Soil at Selate and Kile Solid Waste Dumping Sites

1) Soil pH: The solubility of heavy-metal ions in soil can mainly be influenced by many factors such as soil pH, moisture, temperature etc [59] as indicated in (Table 2). pH of the soils collected from fresh, intermediate and decomposed(old) wastes dumped area at Selate MSW dumping site varied from 6.49 - 6.70, 8.17 - 8.19 and 7.78 - 8.18, respectively. Similarly, soil pH varied with depth at Kile from 6.81-7.19, 7.24-7.5 and 7.75- 8.19 fresh, intermediate and old (decomposed) wastes dumped area of soil sample respectively. Slight similarity of soil pH at both dumping sites might be due to the similar sources and types of waste dumped at both dumping sites, but the pH of soil from control sites were 6.27 to 6.28. Control sites soil pH were lower compared with intermediate and decomposed waste dumping areas at both sites (Table 2). The soil pH value at both dumping sites decreased with increased depth. Different factors like leaching action, soil nature, mechanical composition, etc. might be responsible for the decrease in pH value of soils [31]. According to soil pH ranges set by [47], pH of the soil at both MSW dumping sites were moderately alkaline for intermediate and decomposed (old) wastes dumped area. Higher concentrations of heavy metal in soil at intermediate and decomposed waste dumping area might be the cause for higher pH values of the soils. The recorded pH of soil from decomposed and intermediate dumping area is relatively less than the mean values of similar studies by [34] in Addis Ababa and in Cameroon by [6]. Lower pH of soil from the dumping sites could be attributed to that Harar is less industrialized and populated than Addis Ababa and Cameroon cities. Electrical conductivity (EC): EC is the ability of a material to conduct (transmit) an electrical current and it is commonly expressed in units of millisiemens per meter (ms/m). The recorded results for soil from both dumping sites showed that EC increased as pH decreased. This indicates the effect of pH on soil electrical conductivity. [8], identified that pH and soil moisture content affect the solubility of salts, which also affect electrical conductivity of the soil. Thus, alkaline soil will have less amount of soluble salt. According to [21], lower soil pH indicates larger number of hydrogen ions in the soil. Hydrogen ions can appear in varying amount in the soil environment which can affect the level of electrical conductivity. Higher amount of hydrogen ions in the soil will show a higher rate of electrical conductivity. Hence, low soil pH due to large number of hydrogen ions in the soil may encourage soil electrical conductivity.
Heavy metal concentration in soil: Contaminations of soil at the dumpsites were obviously indicated by higher concentrations of heavy metals relative to the control sites (Table 2). Concentrations of Fe, Pb, Zn, Cu and Cd at Selate dumping site of 0-20 cm of decomposed wastes dumping area were 220.8, 17.88, 63.8, 7.5 and 1.65 mg/kg respectively. But at control sites the recorded results were 39.9, 2.33, 2.00, 1.77 and 0.16 mg/kg at depth of 0-20 cm for Fe, Pb, Zn, Cu and Cd, respectively. These were also similar for Kile dumping site, which show presence of metal containing wastes, contributing enormously to heavy metal pollution. This is in agreement with the results obtained from similar studies by [13], [35], also reported higher levels of some heavy metals in soils around designated municipal solid waste dump site compared to the control site within Port Harcourt and its environment. As showed in (Table 2), the recorded results of accumulated heavy metals in soil showed that zinc, manganese, iron and lead has the higher value at both dumping sites relative to other heavy metals. This suggests that dumped wastes might contain more sources of these metals. From the recorded results concentration of heavy metals in soil were low at fresh dumping area at both sites compare to the decomposed and intermediate ones. This might be due to the initial stage for degradation of fresh wastes and low biochemical process that takes place with fresh wastes. [20, 27] noted that the rate and characteristics of waste vary from one phase to another and reflect the microbial mediated processes. The rate of progress through these stages is dependent on the physical, chemical, and microbiological conditions. In generally, heavy metals like, Lead (Pb), and cadmium (Cd) have no beneficial effects in humans, and there is no known homeostasis mechanism for them [62]. They are generally considered the most toxic to humans and animals; the adverse human health effects associated with exposure to them, even at low concentrations are diverse and include, but are not limited to, neurotoxin and carcinogenic actions [37]. The metals considered in this study include the metals which are micro-nutrient such as iron, zinc and copper and the non-essential/toxic heavy metal which are toxic to plant when present in the soil at concentrations above tolerance level. The non-essential metals i.e., Cr, Pb, Cd, and Co are recognized as health hazardous and all have caused major health problems as a result of environmental pollution [19].

Lead: maximum contamination levels for lead in soil are 0.3-10, 85, 100 and 300 mg/kg for WHO, Dutch, Austria and EU standards, respectively [42, 23, 43]. As showed in (Table 2) concentration of Pb in soil from fresh waste dumping area were low at both dumping sites. Its concentrations were below the standard limits except the WHO limits. Lead concentrations in soil at both sites were also lower than the report of [34] for MSW of Addis Ababa. Concentrations of lead in soil from control area were lower than in soils from waste dumping areas. This indicates continuous dumping of MSW increased hazardous heavy metal concentration at dumping area compared to control area. Higher concentration of lead at dumping area could be attributed to the decomposition of lead containing wastes like disposal of Pb batteries, chemicals for photograph processing, Pb-

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Table 2: pH, EC and heavy metals concentration of soil at solid waste dumping sites
lead at waste dumping sites compared to control sites. At both sites high concentrations of lead in soil were found at upper depth of 0-20cm. Its concentration decreased with increase in depth of soil. These results are in line with finding of [28] who reported higher concentration of lead in surface soils from MSW dumping sites. According to [46], Pb ion is less mobile in soil compared with other heavy metal ions. Lead had been known to have harmful health effects even at lower levels and there is no known safe exposure level. It is appropriate to note that exposure to amount of lead above 0.01 mg/kg is detrimental to health, as it may result in possible neurological damage to fetuses, abortion and other complication in children under three years old [14]. So, the concentration of lead found at both dumping sites of Harar municipal solid waste dumping sites might be harmful for plants, human health and ground water pollution.

4) **Iron**: The standard and accepted level for iron in soil ranges from 100-700 mg/kg [25]. Concentration of iron at Selate site was 220.8 mg/kg in soil from decomposed waste dumping area at 0-20 cm depth, while its concentration was 2.63 mg/kg in soil from fresh waste dumping area at 20-40 cm depth (Table 2). At Kile MSW dumping sites the highest concentration of iron was 173.5 mg/kg in soil from decomposed MSW area at 0-20 cm depth. At both dumping sites high concentration of iron were recorded for soils from decomposed waste dumping areas at 0-20 cm depth. This might be the effect of age and decomposition of waste as a result of temperature, moisture and amount of rainfall. At the control site, iron concentrations in soil also ranged from 29-39.91 and 2.63-3.54 mg/kg for Selate and Kile control sites, respectively as showed in (Table 2), which is much far below the accepted range of iron in soil. Comparing the recorded values at dumpsites to control sites, higher concentration of iron at dumpsites could be attributed to the decomposition of iron containing wastes. Steel scraps are the main sources of iron in the MSW [24]. Iron concentrations in soil of both dumping sites were greater than world health organization standards.

5) **Zinc**: The concentration of zinc in soils were in the range of (0.3-0.91, 64-64.2, 63.8-72.6 mg/kg) at Selate dumping site for fresh, intermediate and decomposed MSW waste areas, respectively (Table 2). At Kile Zn concentrations ranged from 2.72, 12 to 22.97 mg/kg and 42.1 to 65.15 mg/kg for fresh, intermediate and decomposed waste dumped area, respectively. Its concentrations in soil at both sites were within the accepted standards (10 - 300 mg/kg) suggested by [51] but above the limit standards suggested by [30], for Zn in Russia podzols and sandy soils, loose and silty soils, loamy and clay soils. As showed in (Table 2), zinc was more concentrated at 0-20 cm soil depth.

6) **Cadmium (Cd)**: Cd was also detected in soil at both dumpsites as showed (Table 2). The recorded results were 0.32 mg/kg minimum at fresh deposition sites and 1.65 mg/kg at Selate decomposed site. It was more concentrated in dumping sites soil than the control sites. Recorded results for Cd were also greater than WHO standard (0.02 – 0.5 mg/kg) [9]. [60], reported that Cd has highest level of bioavailability in dumpsite. [63], found that the level of Cd, Pb, Hg and As in soils of Netherlands were 0.40, 23.0, 0.07 and 11.0 mg kg⁻¹, respectively. [57], reported that the Cd content of Burayu MSW dumping area was (0.05mg/kg), which is lower than the Cd content in soil at decomposed wastes. But lower than similar study at Addis Ababa MSW dumping site 2.41±2.4 mg/kg [34]. This might be due to differences in generated wastes. For instance, Addis Ababa is more industrialized than Harar City so the wastes generated from Addis Ababa may contain more industrial wastes. In general, the concentrations of Cd in soil from the dumping sites may be attributed to various sources such as automobile tire, dust, paints and dyes. [11], reported that burning of oil and tire, plastic wrappings, paints, dyes, and especially, refuse dumps are the sources of Cd in soil at MSW dumping sites. Cadmium has no beneficial effects in humans, and there is no known homeostasis mechanism for it [62]. It is generally considered the most toxic to humans and animals; the adverse human health effects associated with exposure to it, even at low concentrations. The maximum contamination level of Cd is 0.8, 0.02-0.5, 3 and 5 mg/kg for Dutch, WHO, EU and Austria standards. The recorded results for Cd mean value of the same depth for deferent division of waste at dumping sites were 0.62 mg/kg at 0-20 cm and 0.39 mg/kg at 20-40 cm was below the limits of Dutch, Austria and EU, but it was above WHO standards [42, 23, 43].

7) **Copper**: Concentrations of Cu were 2.18 mg/kg and 2.58 mg/kg in soils from fresh solid waste at Selate and Kile, respectively (Table 2), which were low compared to its concentration in soil from the decomposed and intermediate waste dumping areas. The maximum concentration recorded for Cu was 7.5 mg/kg in soils from decomposed waste dumping area. Its concentrations ranged from 1.77-2.55 mg/kg in soils from the control. The recorded results show that concentrations of Cu in soil at dumping sites were greater than control. This indicates uncontrolled dumping of wastes contributed to increased concentration of Cu in soils at the dumping sites. [17], reported that in normal agricultural soils, total Cu content ranges between 1 and 50 mg/kg and available Cu ranges from 0.1 to 10 mg/kg. The natural range of concentration of copper in soil is (2-100) mg/kg [25]. According to these authors concentrations of copper in soil at both wastes dumping and control sites were within the accepted standard range.
8) **Chromium:** The concentration of Cr in soil at dumping and control sites ranged from 0.11-0.71mg/kg, which was the lowest relative to the concentration of other nine heavy metals analyzed (Table 2). Its concentration was slightly greater than the results reported by [12] for similar study at Yenagoa in Nigeria. However, Cr concentrations in soil at both sites were lower than critical permissible level which is 50 mg/kg for soil recommended for agriculture [26]. Chromium concentrations in soil at both sites were also lower compared to the result (269 mg/kg) reported by [57] in the B2-horizon of soil profile at the northern, industry-free zone of Addis Ababa. The lowest concentration of chromium in soil at both dumping sites in Harar might be absence of chromium source like leather tanning and wood preserving factories in Harar. [40], indicated that wastes from leather tanning, wood preserving and textile factories are the main sources of Cr in soils at waste dumping sites.

9) **Manganese (Mn):** Unexpected results were recorded for Mn at control sites (Table 2). Manganese was more concentrated in soil at control site with mean values of 123.9 and 130.15 mg/kg at 0-20 and 20-40 cm depth, respectively. Manganese concentrations in soil at the depth of 0-20 and 20-40 cm respectively at of both dumping sites were higher than its concentration, (59.74±46.74 mg/kg) reported by [34] in soil at Addis Ababa MSW. According to Thomas (2008) Mn occurs naturally in more than 100 minerals with background levels in soil ranging from 40 to 900 mg/kg, with an estimated mean background concentration of 330 mg/kg. Manganese is released to the environment from industrial emissions, fossil fuel combustion, and erosion of manganese containing soils. So these might be the cause to increase the concentration of manganese at control sites. The concentrations of Mn in soils at both dumping sites were greater than WHO standards.

10) **Nickel (Ni):** as showed in (Table 2) the concentration of Ni in soils at both dumping was lower compared to other heavy metals concentration except Cr. Almost similar results were recorded in soils from waste dumping and the control area at both dumping sites. This might be the absence Ni sources in waste like buttons, zips, coins, dental braces, household appliances tools, artificial joints, jewelry, batteries and hair spray. The concentrations Ni as indicated in (Table 2) were lower compared to similar study at Addis Ababa MSW dumping sites (3-46 mg/kg) reported by [34]. Nickel concentrations in soils at both waste dumping sites were also lower compared to similar study at Kenya, kadhodeki municipal solid waste dumping sites (17.44 mg/kg) [48]. These might be difference in the sources of Ni in wastes generated from Addis Ababa and Kenya are which are more industrialized and populated cities compared to Harar City. However, Ni concentrations in soil at both dumping sites in Harar City were greater than in soil at dumping MSW site at Ogun State in Nigeria (0.07 mg/kg at 0-15 cm and 0.25 mg/kg at 15-30 depth) [4].

C. **Vertical Migration of Heavy Metals**

Pollution problems arise when heavy metals mobilized into the soil solution and take up by the plants or transported to the surface or ground water. The recorded results indicates that the concentration and vertical movements of heavy metals increase with extent of decomposition of wastes. At both dumping sites vertical mobility of heavy metals ions like Fe, Mn, Zn and Cu were increased with the decomposition of wastes (Figures 2 and 3). The figures show that iron cadmium and zinc were more mobile in soil while, lead was less mobile. [55], revealed that metal ions move under conditions where large amounts of water have been applied, or after long-term dumping of waste. Study by [36] on mobility and distribution of Zn, Cd and Pb in soils indicates Zn is relatively mobile in soils. Generally, Cd was present in much smaller concentrations than Zn, even though it is also being considered mobile. Zinc and Cd have similar chemical properties and behavior in soils, but Pb is much less mobile. Pb can also form complexes with organic acids. It is strongly bound to the soil matrix, and soluble Pb complexes will not greatly impact its solubility.

![Figure 2: Metal concentration and migration profiles at dumpsites by depth At Selate Dumping sites with waste age increase.](image-url)
D. Inter-Metal Correlation Analysis and the Statistics T-Test

The relationships between different heavy metal ion concentrations in soil at the dumping sites were analyzed by Pearson’s correlation coefficient. High correlation co-efficient (near +1 or -1) means a good relation between two variables, and zero means no relationship between them at a significant level of 0.05%. r > 0.7 indices strong correlation, whereas r value is between 0.5 and 0.7, it shows moderate correlation between the two parameters. Table 3 showed, that iron correlated positively and significantly with pH (r = 0.96**), Cu (r = 0.94*), Zn (r = 0.97**) and Pb (r = 0.8). pH had the highest correlation with concentration of other trace metal ions in soil. Nickel correlated least significantly with all other heavy metals and pH. Manganese negatively and least significantly correlated with all other heavy metal ions and pH.

The mean value of heavy metal ions concentrations in soil at both dumping sites were compared by t-test at confidence level of 95%. Among two sites of municipal solid waste dumping site, soil sample taken from depth of 0-20 cm, showed (p ≤ .05). Also among two sites of municipal solid waste dumping site soil sample taken from depth 20-40 cm, showed (p ≤ .05), for pH, Zn and Cd [42, 23, 43]. Therefore, reject the null hypothesis that there is no difference in concentration of heavy metals at both dumping sites for depth of 20-40cm.

Table 3 Results of Inter-Metal and pH Correlation Analysis

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<th>Mn</th>
<th>Zn</th>
<th>Cu</th>
<th>Pb</th>
<th>Cd</th>
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IV. CONCLUSION

In this investigation we showed contamination levels at Selate dumpsite with Zn, Mn, Cu, Fe and Pb were at higher, whereas Zn, Fe, Mn, Cu, Pb and Cd were at a higher level at the Kile dumping site. The concentration of Zn (69.7 mg/kg) at Kile dumping sites is the highest from all other recorded heavy metals and Cr (0.07 mg/kg) was the least. The recorded concentrations of heavy metals found in soil were high when compared with their respective concentrations in decomposed municipal solid waste. The top soil layer of 0-
20 cm of decomposed and intermediate wastes dumping division of both dumping sites had more metallic burdens than lower layer depth of 20 - 40 cm. This indicates less vertical migration of heavy metal ions within soil depth. Relative to intermediate and fresh waste dumping areas heavy metals were more concentrated in soil from decomposed waste dumping division. Generally, none of the heavy metals analyzed was higher than the accepted standard except Cd and Pb concentration which were slightly greater than WHO standards. However, the concentrations of all the heavy metals analyzed in soil at dumpsites were higher than their respective concentrations in soil at the control sites. Thus, dumpsites have a significant impact on the environment which could be positive or negative.

REFERENCES


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