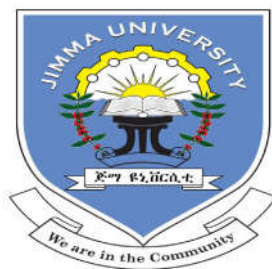JIMMA UNIVERSITY

INSTITUTE OF HEALTH

FACULTY OF PUBLIC HEALTH

DEPARTMENT OF ENVIRONMENTAL HEALTH SCIENCE AND TECHNOLOGY

ASSESSMENT OF THE EFFECT OF SOLID WASTE DUMP SITE ON SURROUNDING SOIL AND RIVER WATER QUALITY IN TEPPI TOWN, SOUTHWEST ETHIOPIA

BY

BESUFEKAD MEKONNEN

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Assessment of the Effect of Solid Waste Dump Site on Surrounding Soil and River Water Quality in Teppi Town, Southwest Ethiopia

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List of Abbreviations and Acronyms

APHA – American Public Health association

BDL- Below detection limit

BOD – Biological Oxygen Demand

CH_4–Methane Gas

CO_2 – Carbon Dioxide

COD – Chemical Oxygen Demand

DS1 – Near to dump site

DS2 – Downstream sample site

EC – Electrical Conductivity

EEPA – Ethiopian Environmental Protection Agency

EU – European Union

FAAS – Flame Atomic Absorption Spectroscopy

GHG – Green House Gas

HNO_3 – Nitric Acid

HCl – Hydrochloric Acid

ISO – International Standardization Organization

KCl – Potassium Chloride

L– Leachate sample site

Mg/L – Mille Gram Per liter

ml – Mille liter

MPI – Metal pollution Index

MSW –Municipal Solid Waste

MSWM – Municipal Solid Waste Management

NA- Not Available

NaCl –Sodium Chloride

PPm – Parts per million

OC- Organic Carbon

OM- Organic Matter

SNNPR – Southern Nations Nationalities People's Region

SWM – Solid Waste Management

TDS –Total Dissolved Solid

USAID – United State America International Development

USDA – United State Department of Agriculture

US EPA – United State of America Environmental Protection Authority

US – Upper stream sample site

UK – United Kingdom

UV – Ultra Violate

WHO – World Health Organization

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Abstract

An increase in the urban population and the rising demand for food and other essentials perpetuate a rise in the amount of waste being generated daily by each household. In low-income countries, this waste is eventually thrown into open dump sites. It can cause severe impacts on human health and the surrounding environment.

This study was aimed at assessing the effect of solid waste dump site of Teppi town on surrounding soil and river water quality.

A total of three surface water, one leachate water samples and four soil samples were collected and were analyzed. Six heavy metals for surface water and leachate samples and four heavy metals for soil samples were measured by flame atomic absorption spectroscopy. Additionally, physical and chemical parameters such as pH, electrical conductivity for both soil and water samples, organic matter for soil samples, TDS, turbidity, nitrate, sulfate, fluoride, potassium, BOD_5, and COD for stream and leachate water samples were analyzed using standard methods of ISO (1995 and 2015), APHA (1992 and1999), and WHO (2004).

pH of soil was slightly basic (pH 8±0.1 up to 8.7±0.21) indicating the influence of solid waste dumped in the area. Similarly, EC was lower in 60 meters (1800±0.5μs/cm) and higher in the other sample sites (3490±0.66-4920±1.04μs/cm). The concentration of heavy metals such as cadmium (0.53±0.01-2.26±0.02 mg/kg), zinc (623.93±0.29-859.41±0.02mg/kg), lead (3.26±0.25-57.560.26mg/kg), and copper (204.06±0.06-337.11±0.01mg/kg) in the sample soils has been found to be higher than EEPA and USEPA guideline values. The concentration of heavy metals such as lead, cadmium, manganese, nickel, copper, and zinc in the leachate water and nickel and manganese in nearby river water, TDS, BOD, COD, and turbidity for both leachate and stream water samples were found to be higher than the EEPA and WHO standard guideline values.

The finding suggested that solid waste open dump site adversely affect soil and water quality in the study area and probable source of human health risks via the food chain. The soil in the area requires Phytoremediation technologies. In addition, appropriate site selection, construction of geo-synthetic layer, erosion preventive brim, and sanitary landfill are recommended.

Keywords: Solid waste, Dumpsite, Leachate, Soil, Water.

CHAPTER ONE

1. INTRODUCTION

1.1. Back Ground of the Study

Waste was an early problem of mankind and a growing one that is a major concern to every nation of the world. In early pre-industrial times, waste generation was not an issue as populations were smaller. Waste was disposed of in the ground where it would turn to compost to improve soil fertility (Birhanu and Berisa, 2015). Waste management issues are coming to the forefront of the global environmental agenda at an increasing frequency, as population and consumption growth result in increasing quantities of waste (Ogundiran and Afolabi, 2008). Rapid population growth and expanding urbanization have caused a drastic increase in the municipal solid waste generation and the variety of the waste composition (Das *et al.*, 2013).

Generally, the higher the economic development and rate of urbanization, the greater the amount of solid waste produced (Al-khatib *et al.*, 2010; Abarca *et al.*, 2013; Alam and Ahmade, 2013). Waste generation varies as a function of affluence, however, regional and country variations can be significant, as can generation rates within the same city. Generation rates, available only for select cities and regions, are approximately 0.5 kilograms per person per day in some cases reaching as high as 0.8 kilograms per person per day (USAID, 2009).

Solid Waste Management is a complex issue throughout the world. In developed countries, the issues of SWM (collection, transportation and disposal) are well understood, accepted and workable (Pires*et al*., 201; Mavakala *et al.*, 2016). Although in developing countries the quantity of solid waste generated in urban areas is low compared to industrialized countries, the MSWM still remains inadequate (Henry*et al*., 2006). Recent events in major urban centers have shown that the problem of waste management has become too complex to handle and has seen dwindling efforts of city authorities, federal governments, state and professionals alike in addressing the issue (Sankoh and Yan, 2013).

As a result, unhealthy disposal of solid waste is one of the greatest challenges facing town planners in developing countries. It is a problem recognized by all nations at the 1992 Conference on Environment and Development and regarded as a major barrier in the path towards sustainability (Agwu, 2012). The problem is especially severe in most low-income countries where poor planning, low awareness level about waste management, handling and lack of adequate resources contribute to the poor state of municipal solid waste disposal system (Moftah et al., 2016).

Open dump approach as solid waste disposal method is an old stage and cheapest of solid waste management system in many parts of developing countries. It is one of the most poorly provided services by municipal authorities as the systems applied are unscientific, outdated, traditional, and inefficient (Kanti et al., 2010; Sankoh and Yan, 2013; Hailemariam and Ajeme, 2014).

In Africa, rapid urban growth since the 1960s has put pressure on the land resources within the area surrounding the cities and has led to the increased generation of waste. Consequently, the problem is forced by the open dump nature of disposing of solid waste especially in the overcrowded areas of most African cities (Turan *et al.*, 2009; Longe and Balogun, 2010; Arukwe *et al.*, 2012). Due to poor and ineffective management the open dump sites turn to sources of environmental problems (Lee *et al.*, 1994; Sankoh and Yan, 2013). Therefore, increased solid waste generation creates the environmental problems in Africa, as many cities are not able to manage it due to institutional, regulatory, financial, technical and public participation shortcomings (Asuma, 2013; Sankoh and Yan, 2013; Haddis *et al.*, 2014; Hafeez *et al.*, 2016).

In Ethiopia with increasing population and urbanization, it remains a major challenge for municipalities to collect, recycle, treat and dispose of increasing quantities of solid waste (Getahun *et al.*, 2012; Berhanu, 2014; Gedefaw, 2015). Likewise, a municipal solid waste disposal problem is a similar scenario in Teppi town. A considerable amount of solid waste ends up in open dumpsite near to residential area and drainage system. Therefore, this study is focused on the assessment of the pollution status of municipal solid waste dumpsite of Teppi town on the surrounding soil and river water quality based on soil and water samples collected from the nearby dump site. In addition, how current practice of open dumping system can be improved to sustainable solid waste disposal system to ameliorate the existing situation.

1.2.   Statement of the Problem

Thousands of tons of solid waste are generated daily in Africa (Asuma, 2013; Sankoh and Yan, 2013). Less than half of the solid waste produced is collected and 95 percent of that amount is either indiscriminately thrown away at various dumping sites on the periphery of urban centers, or at a number of so-called temporary sites and typically empty lots scattered throughout the city (Regassa *et al*., 2011). The indiscriminate and open disposal of waste can cause environmental degradation through introducing different toxicants including heavy metals in the soil and water compartments (Beyene and Banerjee, 2011; Kebede et al., 2016).

According to Bruner *et al*. (1998) the soil pollution arises due to the leaching of wastes from the dump site and the most common pollutants involved metals like copper, lead, cadmium, zinc, etc. Groundwater reservoirs can contaminate surface waters and directly affect amphibians and other wildlife using these surface waters through their food chain.

Surface water contamination plays a significant role as a population stressor because amphibians are dependent on water for reproduction. Rainfall events may alternately dilute toxicity or increase it if the rate of transport increases the flow of contaminants to the surface water (Bruner *et al.*, 1998). Rivers and streams are sinks for municipal solid wastes. Wastes are most often discharged into the receiving water bodies with little or no regard to their assimilative capacities (Abiye, 2008; Ejaz and Janjua, 2012).

pen dumping of MSW is a common practice in Ethiopia and the problem of solid waste disposal is one of the major problems of the community and municipalities (Berhanu, 2014; Gedefaw, 2015). Recent study shows that in most towns municipal solid wastes are disposed of in open spaces without discriminating major residential areas, roadsides, drainage areas, even rivers, river side's and forests. It leads to the introduction of hazardous substances including heavy metals in water and soil ecology (Beyene and Banerjee, 2011; Hailemariam and Ajeme, 2014).

However, there is a need of comprehensive and detail studies about the content of heavy metals and the physical and chemical properties of soil and surface water around solid waste disposal facilities in Ethiopia. There are suggestions for further studies on heavy metals content in the soil profiles and surface water closer to dump sites (Hailemariam and Ajeme, 2014 Kebede et al., 2016). These heavy

metals are adversely affected soil ecology, ground, surface water quality, and ultimately harm to health of living organism by food chain (Pires *et al.*, 2011; Bartoli *et al.*, 2012; Guo *et al.*, 2013; Nazir *et al.*, 2015; Rastegari *et al.*, 2017).

Similarly, Teppi town is characterized by rapid population growth caused by natural increase and migration. Such rapid increase in population together with the rapid development of the town has produced increasing volumes of solid waste. Indiscriminate solid waste disposal is actually a menace and embarrassment to Teppi town. Considerable percentage of solid wastes generated in Teppi town is disposed of unapproved dump site and in water ways (drainage system) or in open site near to residential area which adversely affect environmental friendliness. In fact, solid waste poses various threats to public health and adversely affects soil and water especially when it is not appropriately disposed (Agwu, 2012). Due to high rainfall experienced in the study area, the dump site becomes washing out and the leachate with its pollutants draining into the Shay Wenz River.

Fresh water is an imperative resource for people and provides many provisioning such as regulatory, cultural and ecosystem services for the community and the world in general (Troyer *et al.*, 2016). Similarly, the river near to Teppi town solid waste dump site is largely used by the local communities for irrigation, bathing and drinking purpose. Therefore this paper aimed at assessing on improper disposal of solid waste and its pollution impacts on surrounding soil and water quality in Teppi town, southwest Ethiopia.

1.3. Significance of the Study

Improper management of municipal solid wastes leads to substantial negative environmental impacts such as pollution of soil and river water (Nartey *et al*., 2012; Pastor and Hernandez, 2012). Improper management of solid waste is also the problem of Teppi town which results in pollution of water and soil. However, as far as my knowledge there is no any study that has been conducted in the town that indicates the extent of the problem. Therefore, this study will try to fill the gaps by assessing factors and point out the problem of soil and river water quality resulting from pollution emanating from the indiscriminate disposal of solid wastes in the open dump site.

The result of this study will be used:

➤ To plan appropriate solid waste disposal system for the town municipality.

➤ As a source of information about the outcomes of inappropriate dumping of solid wastes for the municipality, the communities and non-governmental organization to solve environmental and human health related problems.

➤ As a baseline data for further studies.

CHAPTER TWO

2. LITERATURE REVIEW

2.1. Solid Waste Management

A cornerstone of sustainable development is the establishing of affordable, effective and truly sustainable waste management practices in developing countries. It must be further emphasized that multiple public health, safety, and environmental co-benefits accrue from effective waste practices which concurrently prevent water and soil contamination, improve the quality of life, and promote public health (Shari *et al*., 2016).

The legislation of MSWM is focused on protection of the health of the population, promote environmental quality, develop sustainability, and provide support to economic productivity. To meet these goals, sustainable solid waste management systems must be embraced fully by local authorities in collaboration with both the public and private sectors (Pires *et al*., 2011). SWM is a complex issue throughout the world. In developed countries, the issues of SWM (collection, transportation, and disposal) are well understood, accepted and workable (Pires *et al*., 2011; Mavakala *et al*., 2016). Although in developing countries the quantity of solid waste generated in urban areas is low compared to industrialized countries, the MSWM still remains inadequate (Henry *et al*., 2006). Recent events in major urban centers have shown that the problem of waste management has become too complex to handle and has seen dwindling efforts of city authorities, federal governments, state and professionals alike in addressing the issue (Sankoh and Yan, 2013).

Likewise, the Federal Democratic Republic of Ethiopia has ratified several international conventions that have meaningful implication to solid waste management in the country (Gedefaw, 2015). Furthermore, the solid waste management proclamation (No. 513/ 2007) article 14 stated that each urban administration shall conformity with the relevant environmental standard, ensure that solid waste disposal sites are constructed and properly used. Moreover, with objective to promote community participation in order to prevent the adverse effect and to enhance the benefits result from solid waste. The solid waste management action plans designed and implemented at the lowest administration unit of administration to ensure community participation. Accordingly, the objective of the proclamation is

to enhance at all level capacities to prevent the possible adverse impacts while creating economically and socially beneficial assets out of solid waste management. However, due to low awareness level about waste management, resources, and implementation of the proclamation most of the towns of Ethiopia are torment from the adverse effects of improper disposal of solid waste on urban soil and surface water quality (Beyene and Banerjee, 2011; Kebede et al., 2016).

2.2. Soil and Water Contamination

2.2.1. Soil Contamination

The Soil is a reservoir of many heavy metals from discharge of untreated municipal solid wastes. Metals exist in the soil in various forms and most of them have toxic effects on living organisms when exceeding certain concentration limits. Heavy metals exhibit toxic effects towards soil biota by affecting key microbial processes and decrease the number and activity of soil microorganisms. Heavy metals can move in soil profile vertically or horizontally from the point where they are accumulated to other areas via different mechanisms (Prechthai *et al*, 2008; Jiwan and S, 2011).

According to Bartoli *et al.* (2012) the physical and chemical characteristics of the soil system influence the transformation, retention, and movement of pollutants through the soil. Some metals tend to be relatively strongly adsorbed by soil constituents and their mobility and bioavailability depend on the soil condition. Other studies by Violante *et al.* (2010) and Shiva Kumar and Srikantaswamy (2014) shows not all soil properties have equal influence on the mobility and availability of a particular metal. For each metal it is therefore important to know the dominant soil property that will control the behavior of that metal in that particular soil. With regard to bioavailability, the following metal fractions have an important role in soil such as metals in soil solution; precipitated metals; metals bound to clay minerals, oxides and hydroxides, organic matter, and metals in the soil mineral matrix.

 Different international scholars have linked the sorption behavior of heavy metals in soils with such soil properties as pH and soil organic matter (SOM), particle size (clay), and oxides. Besides soil pH, which is the factor influencing the mobility/availability of heavy metals to the greatest extent, the content and quality of soil organic matter are considered to be the principal properties determining the retention capacity of soils. Generally, organic matter contains different types of functional groups such as phenolic group (-OH) which are capable of forming complex with metals. Organic matter may influence the concentration of heavy metals in soil by different processes such as release of heavy

metals containing organic matter into the soil and extraction of heavy metals by organic matter in the soil forming organic complexes etc. (Dube *et al.*, 2001; Aydinalp and Marinova, 2003; Bradl, 2004; Fern *et al.*, 2007; Haberhauer, 2007).

Various studies have documented the impact of the constituents of solid waste from dump sites. High level of heavy metals in particular Cd, Zn and Pb were reported to emanating from Ilorin Metropolis dumpsite (Abdus-Salam, 2009). A study by Adelekan and Alawode on contributions of municipal refuse dumps to heavy metals concentrations in the soil profile in Ibadan Nigeria recorded that the values of Cd, Co, Pb, Ni in the dumpsites soil samples ranged from 0.75-16.30; 3.45-21.00; 45.00-624.50; 4.35-49.80 mg/kg, respectively. Another study by Akinbile at Nigeria landfill shows all analyzed heavy metals recorded higher concentration than the limit prescribed by FAO.

A study to assess the heavy metal contamination in soil due to leachate migration from an open dumping site shows heavy metals like Pb, Zn, Cd, and Mn in soil sample indicates that there is appreciable contamination of the soil by leachate migration from an open dumping site (Gandhimathi, 2013). Another study by Ideriah on heavy metal contamination of soils and vegetation around solid waste dumps in Port Harcourt, Nigeria indicate that solid wastes contributed to the levels of heavy metals in soils and vegetation (Ideriah et al., 2010). A study by Haliru et al. on environmental burden of heavy metal contamination levels in soil shows above the maximum permissible heavy metal concentration levels in soil set out by EU, UK and USA (Haliru et al., 2014).

Another study conducted in Islamabad city, Pakistan on open dumping of municipal solid waste and its hazardous impacts on soil and vegetation diversity shows soils at the disposal sites revealed high pH and EC regime in comparison to control sites. Various heavy metal concentrations i.e., Lead (Pb), copper, nickel, and zinc were also found to be higher at the dumping sites (Ali and Yasmin, 2014). Another study by Abdourahamane et al. at Maradi city (Niger Republic) shows the pH of dump sites were mainly alkaline, indicator of active landfill/dumpsite and trace elements such as Zn, Pb, and Cd were higher in dump site as compared with control sample (Abdourahamane et al., 2015). Another studies conducted in Addis Ababa and Adama solid waste dump site shows an increment in the contents of cadmium, lead, and chromium by 3.67, 17-1833.5 and 19.68 mg/kg respectively in the nearby agricultural soil (Alemayehu, 2001; Beyene and Banerjee, 2011; Asmamaw *et al.*, 2016).

2.2.2. Water Contamination

Contamination of water bodies has become an issue of serious environmental concern. Rivers due to their role in carrying off the municipal and industrial wastewater and runoff from agricultural land in their vast drainage basins are among the most vulnerable water bodies to pollution (Singh *et al.*, 2005; Milovanovic, 2007). Literature survey shows that rivers in urban areas have also been associated with water quality problems because of the practice of discharging of untreated municipal and industrial wastes into the water bodies which leads to the increase in the level of metals in river water (Islam *et al.*, 2015; Maanan *et al.*, 2015).

The physical hazards are the dissolved solids and suspended solids. The chemical hazards are the copper, manganese, lead, cadmium, phosphate, nitrate, etc. As the public health concern, drinking water should be free from physical and chemical hazards. The people in and around the dumping site are depending upon the groundwater and surface water for drinking and other domestic purposes (Raman and Narayanan, 2008a; Verma and Dwivedi, 2013).

Leachate from open dump sites usually contains both biological and chemical constituents (Stra *et al.*, 2009; Gandhimathi, 2013; Dervisevic *et al.*, 2016). Organic matter, decomposing under aerobic conditions, produces carbon dioxide which combines with the leaching water to form carbonic acid (Nehrenheim *et al.*, 2009). This, in turn, acts upon metals in the refuse and upon calcareous materials in the soil and rocks, resulting in increasing hardness of the water (Yusof *et al.*, 2009).

Under aerobic conditions, bacterial action decomposes organic refuse, releasing ammonia, which is ultimately oxidized to form nitrate. In both landfills and open dumps, where decomposition is accomplished by bacterial action, the leachate has a high biochemical oxygen demand. Toxic chemicals that have high concentrations of trace elements, nitrate, sulfate, and phosphate derived from the waste in the soil can filter through the dump and contaminate both the ground and surface water (Nirmala Dharmarathne, 2013). Leachate contamination of soil and surface water are the environmental issues connected with the dumpsites (Martinho *et al.*, 2009; Nordmark *et al.*, 2009; Ruiz *et al.*, 2009; Akinbile, 2011; Persson *et al.*, 2015).

A study conducted in Abbottabad, Pakistan on effect of landfill leachate on the stream water quality shows the parameters exceeding the allowable limits of WHO included pH, TDS, BOD, COD, and

heavy metals like Pb, Cd, and Cu were released from the leachate into the Salhad stream which might affect the sustainability of the aquatic life (Maqbool et al., 2011). A study by Bouzayani et al. on leachates draining from controlled municipal solid waste landfill detailed geochemical characterization and toxicity tests shows ladfill leachates should not be discarded into the environment (soil or surface water) without prior treatment (Mavakala *et al.*, 2016).

Another study conducted by Hasan et al. showed that heavy metal concentrations in the marine surface water generally exceed the criteria of international marine water quality. Moreover, both the contamination factor and pollution load index values suggested the elevation of heavy metals concentration in surface water due to improper disposal (Hasan *et al.*, 2016).

In particular, the average concentration of Zn, Cr, Pb in leachate and surface water nearby the landfill site at Delta state, Nigeria shows higher than the limits prescribed by WHO (2004) (Asuma, 2013). Another study conducted in Matuail landfill site, Dhaka shows high concentration of TDS (734 ppm), COD (1631 ppm), and certain heavy metals such as Ni (1.05 ppm) and Cr (0.74 ppm) and have very high potential for contaminating ground and surface water (Azim *et al.*, 2011).

A study by Raman and Narayanan in India indicated that the water samples collected from the dumpsite had appreciably high level of temperature, pH, electrical conductivity, total dissolved solids, nitrate, sulphate, phosphate and the metals like potassium, copper, manganese, lead, cadmium, chromium, and nickel (Raman and Narayanan, 2008). Another study by Islam et al. at Bangladeshi on heavy metal pollution in surface water and sediment: a preliminary assessment of an urban river shows the level of studied metals exceeded the safe limits of drinking water (Islam et al., 2015).

Another study conducted by Zafar and Alappat in New Delhi, India shows that the river water quality is affected by the presence of landfill surface runoff. Its impact can be seen in the region where the drains are meeting the river (Zafar and Alappat, 2004). Another study on impact of poor municipal solid waste management practices and sanitation status on water quality and public health in cities of the least developed countries: the case of Juba, South Sudan prove that TDS showed very high values with range of 47 – 123 mg/100ml which is far beyond the USEPA and WHO recommended 500 ml/l and the EC was not so high; ranges between 59μs-201μs/cm which is slightly above the recommended 160 μs/cm.

A study by Longe Kanti et al. on environmental quality in and around municipal solid waste dumpsite shows moderately high concentrations of heavy metal in groundwater, likely indicated that the groundwater quality has been significantly affected by leachate percolation and the results emphasized that there is an urgent need to adopt certain measures at the landfill site for the protection of environmental quality in and around Mathkal landfill site (Kanti *et al.*, 2010).

In Ethiopia, there are researches done to investigate contamination of surface water due to open solid waste disposal sites of Addis Ababa. It shows an increment in the contents of chromium, cadmium, and lead by 99.48%, 95.4%, and 93.9% respectively at the outlet of a leachate stream was revealed (Alemayehu, 2001; Beyene and Banerjee, 2011). A high amount of nitrate, sulfate, BOD, COD, and TDS, chloride, and sulphate besides high concentration of cobalt, nickel and zinc and other numerous compounds were investigated from nearby surface water at Addis Ababa dump site (Alemayehu, 2001; A.Abiye, 2012).

2.3. Scope of the Study

The scope of the study is focused on investigating the concentration of leachate emanates from the solid waste dump site and pollutants that change soil and surface water quality nearby solid waste dump site in Teppi town.

2.4. Research Questions

➢ What are the characteristics of leachate that emanating from solid waste dump site?
➢ Is there a change in the quality of soil due to the presence of dump site?
➢ Is there a change in the quality of river water due to the presence of dump site?

CHAPTER THREE

3. OBJECTIVES

3.1. General Objective

The general objective of this study is to assess the effect of solid waste dump site on the surrounding soil and river water quality in Teppi town, southwest Ethiopia.

3.2. Specific Objectives

- ➢ To determine the characteristics of leachate emanating from the dump site.
- ➢ To assess the level of soil pollution around the solid waste dump site.
- ➢ To investigate the level of water pollution in the catchment area of the dump site.

CHAPTER FOUR

4. METHODS AND MATERIALS

4.1. Study Area

Teppi is a town in southwest Ethiopia and well known by the production of coffee and spice. The town is located in 621 km south of Addis Ababa, 226 km southwest of Jimma town and 52km of Mizanteferi. The town has a latitude and longitude of 7°12′N 35°27′E with a mean elevation of 1,097 meters above sea level. The town is said to be named after a Majangir man who once had been live in the large tree that stood in the marketplace. According to Ethiopia central statistics authority, a population projection 45,560 population was live in Teppi town.

The Cenozoic and Proterozoic volcanic sediments underlie most parts of the southwestern Ethiopia. Generally, the soils of the area are red or brownish ferrisols derived from the volcanic parent material. The prevalence of high rainfall has masked other soil forming factors and hence, very similar soils have developed on a variety of parent materials. Other soil groups in the area include aerosols, vertisols, and camisoles (Source: Teppi soil research center, 2016).

The mean annual rainfall is estimated to be over 2200 mm. The mean maximum temperature is estimated to be between 25°C and 34°C, and the mean minimum is estimated to be between 10°C and 15°C. The rainfall distribution is unimodal, with the highest rainfall between June and September. Rain falls has throughout the year, with monthly minimum and maximum of about 70 and 220 mm. It also has a relatively long growing season of well over 250 days per year. The average temperature of the warmest month 32°C and the average temperature of the coldest month is 12°C (Source: Teppi soil research center, 2016).
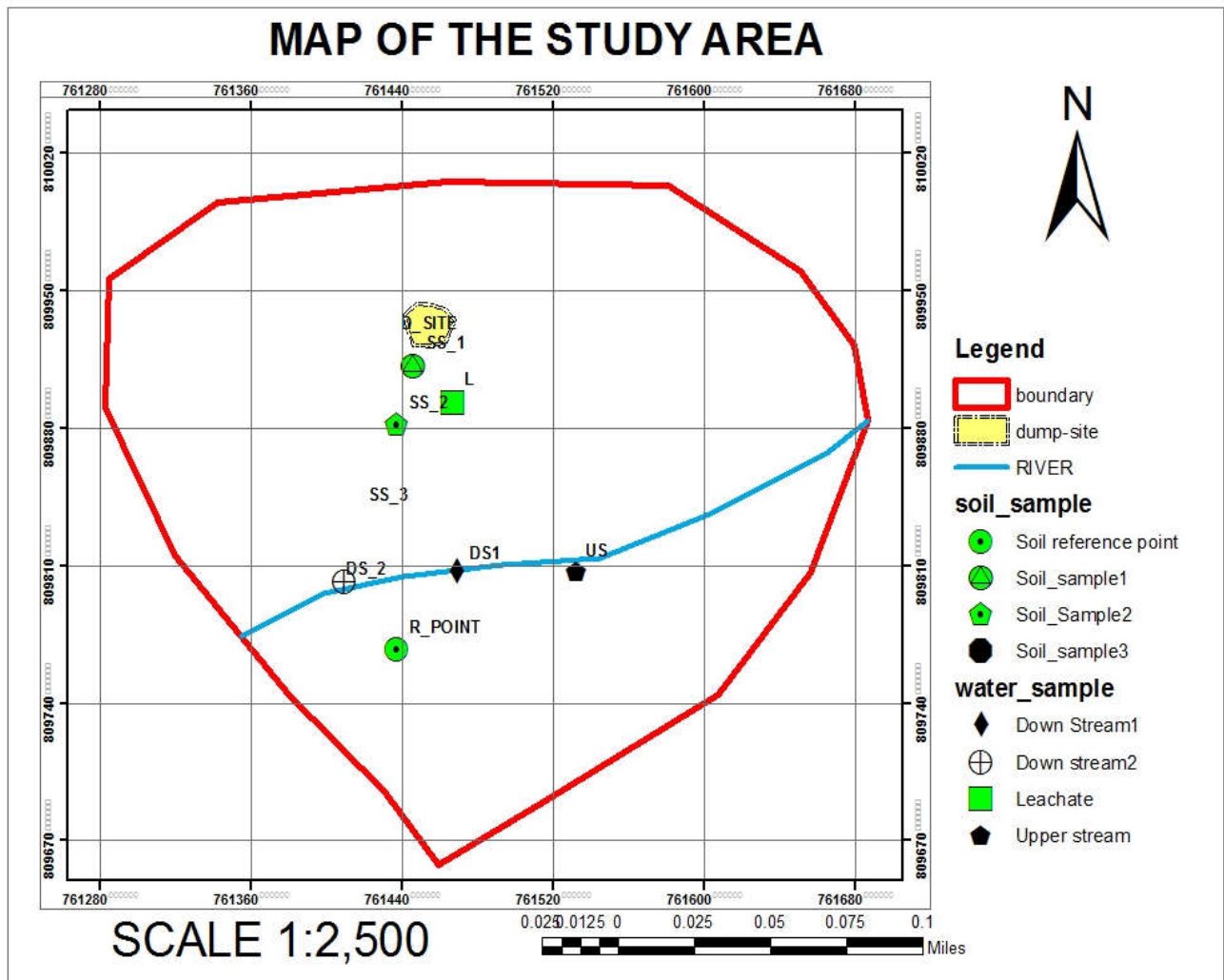
Figure 1: Sampling location for soil and water samples at Teppi town solid waste dump site.

4.2. Study design and period

Experimental study was used to characterize the leachate quality of solid waste dump site of Teppi town and to determine the quality of soil and surface water in the nearby dumpsite. The study was conducted from March to Jun 2017.

4.3. Samples collection and treatment

4.3.1. Soil Samples Collection and Treatment

The dump site was physically observed and the sample sites were demarked. The sample sites were selected by transects through simple random sampling method towards gully erosion based on US EPA (1992) soil sampling protocol. The study was conducted in the dry season. The sample points were being located at 10 meters, 30 meters, and 60 meters away from the periphery of dump site (US EPA, 1992 ; Akoto *et al*., 2008; Ideriah *et. al., 2010*; Bouzayani *et al*., 2014; Kebede *et al*., 2016).

Figure 2: Solid waste dump site at Teppi town.

Soil samples were collected from the dump site by stainless steel hand augur (USDA, 1982; US EPA, 1992).

Figure 3: Soil sampling by hand auger at Teppi town solid waste dump site.

Soil samples were taken at a depth of 0.5-20cm from each sample points. The top 0.5cm of surface soil was removed before the samples were taken (USDA, 1982; US EPA, 2002; Kebede *et al*., 2016).

Meanwhile, the representative samples were coded and leveled on information sheet and attached to the sample polyethylene bag. Then the collected samples were thoroughly mixed on the net polyethylene sheet and transported to SNNPR bureau of agricultural development Teppi soil testing laboratory center. Then air dried for 72 hours (US EPA, 2002; Kebede *et al*., 2016) in Teppi soil testing laboratory center drying bed.

Figure 4: Soil samples in drying bed at soil laboratory.

The soil samples were disaggregated with mortar and pestle finely powdered as well as thoroughly mixed together with other precautions to prevent contamination of the samples.

Figure 5: Soil samples treatment and preparation at laboratory.

In the above figure 5 A represent air-dried soil sample, B represent grinding of soil sample, C represent the crushed soil was sieved through a 2 mm sieve, and D represent subsample < 2mm mesh size was used for analysis. The soil pH and electrical conductivity (US EPA, 2002; Raman and Narayanan, 2008; Beyene and Banerjee, 2011; Kebede *et al*., 2016) were analyzed in Teppi soil testing laboratory

center and the total heavy metals and organic matter were detected in JIJE analytical testing service laboratory in Addis Ababa, Ethiopia with appropriate handling.

4.3.2. Water Samples Collection and Treatment

Water samples were taken through purposive random sampling techniques. Optimum amount of river water samples (1-liter) were collected from three different sample points upper stream from dump site (US) 100 meters far from the dump site, near to the dump site (DS1), and 100 meters far from the dump site in downstream direction (APHA, 1992; Hossain *et al*., 2014; Kumar *et al*., 2017).

These water samples were taken from the places where the river has laminar flow pattern in order to keep uniformity of samples and obtained at a depth of 10-15 cm below the surface water to avoid floating debris and put into 1-liter polyethylene bottles. The leachate sample (L) was taken from the place near to dump site (APHA, 1992; Hossain *et al*., 2014; Kumar *et al*., 2017). At each sample points, two sets of water samples were collected into separate pre-cleaned 1-liter polyethylene bottles. 2.0 ml of concentrated HNO_3 was added to one of the bottles to bring the pH < 2 in order to prevent adsorptions of heavy metals on the bottom of sample containers. The acidified samples were used for elemental analysis and the non-acidified samples were used for biological analysis (APHA, 1992; Nartey *et al*., 2012; Hasan *et al*., 2016).

Figure 6: water sampling at Teppi town sold waste dump site.

4.4. Study variables

4.4.1. Independent variables

Horizontal distance from the periphery of the dump site for soil samples (10m, 30m, and 60m).

Location from the dump site for water samples (upper stream, near to the dump site, downstream, and leachate from the dumpsite).

4.1.2. Dependent Variables

Physico-chemical properties of soil (pH, electrical conductivity, and organic matter).

Heavy metals concentrations in soil (lead, cadmium, copper, and zinc).

Physico-chemical properties of stream water and leachate (pH, EC, temperature, BOD_5, turbidity, pH, COD, electrical conductivity, TDS, nitrate, sulfate, fluoride, and potassium).

Heavy metals concentration in water samples (lead, cadmium, copper, nickel, manganese, and zinc).

4.5. Analytical Methods

4.5.1. Soil Samples Analysis

Soil electrical conductivity was analyzed by 1:2.5 soil-to-water extraction methods (USDA, 1982; Reeuwijk, 1992; Houba *et al.*, 1998). The extract was measured by digital EC meter (H12300 EC/TDS/NaCl meter, HAWA instrument, Romania, model) and pH was measured with pH meter (pH-016 model) by using a glass electrode and detail procedures were attached in annex 1.

Determination of organic carbon in the soil was carried out through the spectrometric method of modified ISO 14235 (2015). Soil organic matter is oxidized under standard conditions with potassium dichromate (in excess) in sulfuric acid. The dichromate ions, which color the solution orange-red, were reduced to Cr^{3+} ions which color the solution green. A measured amount of potassium dichromate was used in excess of that needed to destroy the organic matter and the excess determined by titration with ferrous ammonium sulfate solution, using diphenylamine indicator to detect the first appearance of un-oxidized ferrous ion. Assumed that the oxidation of one carbon atom of the organic matter produces four electrons, there is a direct relationship between the Cr^{3+} formed and the amount of organic carbon. 1.724 was used for conversion factor from % OC to % OM (Kuryntseva *et al.*, 2016) and detail apparatus, reagents and procedures were attached in annex 1.

Heavy metals (lead, cadmium, copper, and zinc) extraction from soil samples were performed by an aqua regia digestion based on ISO 11466 recommended method (ISO, 1995). The air-dried sample was extracted with a hydrochloric/nitric acid 3:1 mixture by standing for 16 hours at room temperature, followed by boiling under reflux for 2 hours. The extract was then clarified and made up to volume

with nitric acid. The extract thus prepared was ready for the determination of elements by flame atomic absorption spectroscopy (PG 990, China model) (ISO, 1995; Sastre *et al.*, 2002; Samuel *et al.*, 2005; Akan *et al.*, 2013) and detail apparatus, reagents and procedures were attached in annex 2.

4.5.2. Water Samples Analysis

In situ measurement of different parameters was held by using a digital portable multi-parameter probe (Micro 800 plain test, UK model**)**. In addition, Electrical Conductivity (EC) and Total Dissolved Solids (TDS) were measured by EC/TDS meter (Micro 800, Plain test, Wage tech company, UK, model) and turbidity was measured by turbidity meter (plain test, UK model).

Figure 7: In situ measurement of water samples at Teppi town solid waste dump site.

At laboratory level, nitrate, sulfate, and fluoride were be measured by the spectrometric method and the concentration was estimated by UV visible spectrophotometer (Plain test 7500, Wag Tech Company, UK model) (WHO, 2004; Osei *et al.,* 2011; Wagtech, 2011; Nartey *et al*., 2012) and detail apparatus, reagents, and procedures were attached in annex 3.

Figure 8: Laboratory measurement of the chemical parameter of water samples.

Some selected trace elements (copper, zinc, lead, cadmium, nickel, and manganese) were analyzed through in an unfiltered sample after vigorous digestion, or the sum of the concentrations of metals in the dissolved and suspended fractions. Note that total metals were defined operationally by the digestion procedure of APHA 3111c air/ acetylene oxidizing flame method (APHA, 1992) and the concentration of total elements was measured by flame atomic absorption spectroscopy (PG-990, China model) detail apparatus, reagents and procedures were attached in annex 1.

Figure 9: FAAS used for heavy metals measurement in JIJE analytical test service laboratory at Addis Ababa.

The dissolved oxygen content in the sample was measured by using azide modification of the titrimetric iodometric method (Section 4500-O.C). Dissolved oxygen was measured initially and after incubation for 5 days and the BOD_5 was computed from the difference between initial and final dissolved oxygen. Because the initial dissolved oxygen was determined shortly after the dilution was made, all oxygen uptakes occurred after this measurement was included in the BOD_5 measurement.

Among the different values of BOD_5 obtained for a sample select that dilution showing the residual dissolved oxygen of at least 1 mg/l and a depletion of at least 2 mg/l (APHA, 1999) and detail apparatus, reagents and procedures were attached in annex 3.

COD was determined through using potassium dichromate in an open reflux method. A sample was refluxed in strongly acid solution with a known excess of potassium dichromate ($K_2Cr_2O_7$). After digestion, the remaining unreduced $K_2Cr_2O_7$ was titrated with ferrous ammonium sulfate to determine the amount of $K_2Cr_2O_7$ consumed and the oxidizable matter was calculated in terms of oxygen equivalent (APHA, 1999) and detail apparatus, reagents and procedures were attached in annex 3.

4.6. Data Quality Management

To ensure reliability and validity during field and experimental work, different strategies were employed. First, Field & laboratory instruments were standardized. In addition, every precaution should be taken the manufacturer's recommendations and calibration of the instrument strictly followed the specific procedure provided for the operation and calibration of instruments available in the laboratories. Second, hand auger was washed using distilled water prior to use and before shifting to the next soil sample site. Soil sample collection and preservation was made based on USEPA (1992) soil sample quality assurance user´s guidance. In addition, sample labels were properly completed including the sample identification code, date, stream name, and sampling location, and then placed into the sample containers and polyethylene bags. Storage and shipment of water samples were performed in manners that maintain samples quality. The water samples were cooled to 4°C/72h ice peg (RCW 25, Italy Model) as soon as after samples were collected (APHA, 1992; Raman and Narayanan, 2008b; Prechthai *et al*., 2008; Nartey *et al*., 2012).

Figure 10: Model of Ice peg used for water and leachate samples preservation.

The outside of the containers and polyethylene bags were labeled with the same information. In addition, the sampling plan was coordinated with the laboratory so that proper sample transport, receipt, storage, analysis, and custody arrangements were provided. Finally, the results were checked three times (triplicate) in order to yield the most reliable data.

4.7. Data Analysis

4.7.1. Soil Data Analysis

The soil data were analyzed statistically using Origin pro version 8.0 computer software packages and Microsoft Excel. Analysis of variance (ANOVA) was used to assess whether the mean values of heavy metals in soil samples varied significantly between distances from the dump site, possibilities less than 0.05 ($p < 0.05$) was considered statistically significant. The analyzed data was presented by using figures and tables. All the mean values were compared with heavy metals limits in soil prescribed by Ethiopian Environmental Protection Agency and US EPA standards.

4.7.2. Stream Water and Leachate Data Analysis

Analysis and interpretation of all water chemistry data were carried out using Origin pro 8.0 version package software and Microsoft Excel. Analysis of variance (ANOVA) was used to assess whether the concentrations of heavy metals, physical, and chemical parameters varied significantly between locations from the dump site, p-value < 0.05 was considered statistically significant. The analyzed data

was presented by using figures and tables. All the mean values of the findings were compared with surface water guideline values of Ethiopian Environmental Protection Agency (2003) and World Health Organization (2004).

4.8. Ethical Consideration

Written consent was obtained from Jimma University, faculty of public health ethical review board and the Department of Environmental Health Science and Technology, Zonal, Town, district and Keble administrations. Additionally, an informed written consent was obtained from the study subjects.

4.9. Dissemination of the Finding

The finding of the study submitted to the Jimma University, Faculty of Public Health, and Department of Environmental Health Science and Technology. The finding presented during thesis defense, as a partial fulfillment of the requirement of masters degree in Environmental Science and Technology. Finally, attempts will be made to present the finding on scientific conferences and to publish it in peer reputable journal.

4.10. Limitation of the Study

The thesis lacked seasonal dynamics of pollution status in the soil, water, and leachate quality with other compounding factors. The thesis doesn't show the town waste generation rate, composition of solid waste, collection, and transport system.

CHAPTER FIVE

5. RESULTS

5.1. Soil pH, EC and organic Matter

pH is a term used universally to express the intensity of the acid or alkaline condition of a solution (Hailemariam and Ajeme, 2014). The mean values of pH in the study area were between 8±0.1 and 8.7±0.11 slightly basic in nature. The sample points 10 meters, 30 meters and 60 meters far away from the dump site were found to be 8.7±0.11, 8.4±0.1 and 8.0± 0.1 respectively (slightly basic) and the means were significantly different at P-value < 0.05 level.
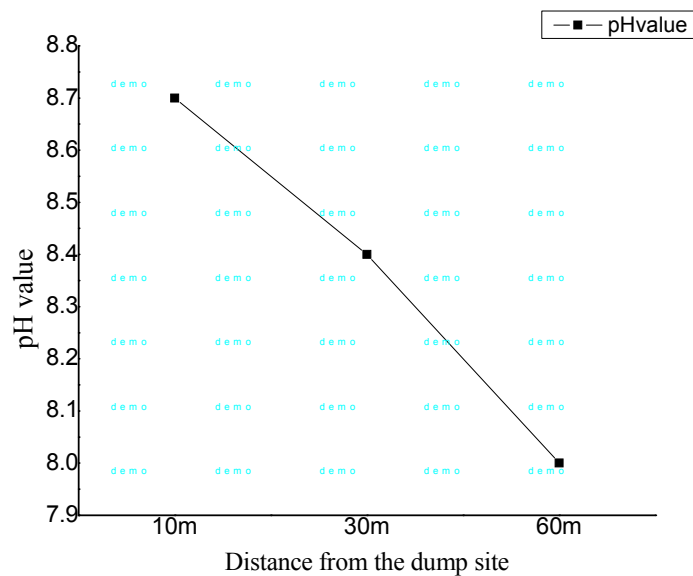
Figure 11: Soil pH at Teppi town solid waste dump site.

Figure 13 shows the electrical conductivity measurements during the experiment. The conductivity of soil in the sample was recorded between 1800±0.5 and 4920±1.04μs/cm. The sample site 60m far from the dump site was measured the lowest value which shows 1800±0.5 μS/cm compared to the other sites which revealed 4920±1.04, 3490±0.6 μS/cm respectively and at P-value < 0.05 levels the means were significantly different.
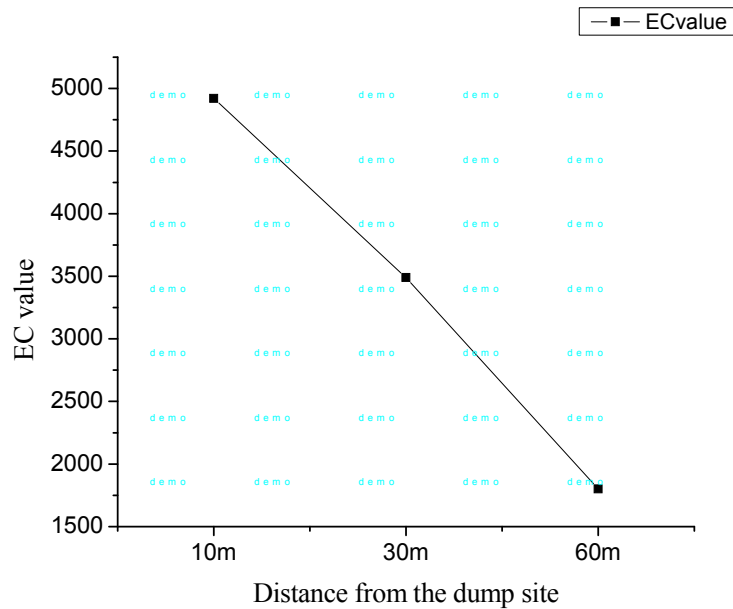
Figure 12: EC values of soil samples at Teppi town solid waste dump site.

Organic matter was recorded 8.05%, 5.1% and 4.95% in 10 meters, 30 meters, and 60 meters respectively far from the dump site.

5.2. Heavy Metals Result of Soil Samples

Table 1: Concentration of Pb, Cd, Zn and Cu in soil around Teppi town sold waste dump site along different sample sites.

Parameters	10 meters	30 meters	60 meters	EEPA Standard	USEPA Standard
Lead(mg/kg)	57.56±0.26	52.21±0.02	3.26±0.25	40	50
Cadmium(mg/kg)	2.26±0.02	1.6±0.01	0.53±0.01	0.5	1.4
Copper(mg/kg)	337.11±0.05	286.11±0.2	204.06±0.05	500	80-200
Zinc (mg/kg)	859.41±0.2	826.45±0.01	623.93±0.29	500	200-300

The above table 1 shows the lowest (3.26±0.25mg/kg) mean values of lead were recorded in 60 meters far from the dump site; in the contrary highest value was measured in 10 meters distance from the dump site (57.56±0.26 mg/kg). Moreover, the difference was statistically significant at P-value < 0.05. Cadmium was one of the heavy metals analyzed in the dump site. It was found to be 2.26±0.21, 1.6±0.01 and 0.53±0.01 mg/kg in 10 meters, 30 meters, and 60 meters far from the periphery of dump site respectively. The means were significantly different at P-value < 0.05 level.

Considering all samples obtained at the dump site copper ranged from the minimum found to be 204.06±0.05 mg/kg in the 60 meters far from the dump site. In the contrary highest mean values of copper were found in 10 meters and 30 meters far from the periphery of dump site shows 337.11±0.05 and 286.11±0.2 mg/kg respectively and the means were significantly different at P-value < 0.05 level. The highest mean values of zinc were found in 10 meters and 30 meters away from dump site which shows 859.41±0.2 and 826.45±0.01mg/kg respectively. The lowest mean concentration of zinc was revealed in 60 meters away from the dump site 623.93±0.29 mg/kg and the means were significantly different at P-value < 0.05.

5.2.1. Soil Metal Pollution Index

As Haliru *et al*. (2014) adapted from Lacatusu, (2000), the differences between soil contamination range and soil pollution range are given by the metal contamination/ pollution index (MPI).

$$MPI = \frac{Concentration\ of\ heavy\ metals\ in\ samples}{Concentration\ in\ the\ reference\ value}$$

This index value represents the ratio between the heavy metal content effectively measured in soil by chemical analysis and reference value obtained from the EEPA reference (guideline) value. The values of contamination/pollution index of soil greater than 1 (> 1), define the pollution range and those less than 1 (<1) define the contamination range (Lacatusu *et al.*, 2000; Hu *et al.*, 2013; Haliru *et al*, 2014).

The two ranges of values were divided into interval of values < 0.1 as very slight contamination, 0.10 – 0.25 as slight contamination, 0.26–0.5 as moderate contamination, 0.51–0.75 as severe contamination, 0.76–1.00 as very severe contamination, 1.1–2.0 as slight pollution, 2.1 – 4.0 as moderate pollution, 4.1 – 8.0 as severe pollution, 8.1–16.0 as very severe pollution and > 16.0 as excessive pollution

(Lacatusu, 2000; Haliru *et al*, 2014). Comparison of the mean concentration values of heavy metals in soil obtained from this study was also done to determine the extent of contamination/pollution with the international maximum permissible levels of heavy metals in soil.

Table 2: Metal pollution index for soil sample at 10 meters distance from the periphery of Teppi town solid waste dump site.

Heavy metal Mg/kg	Depth (cm)	Site 10m Mean(mg/kg)	EEPA (mg/kg)	MPI	Class interval According to Lactusu(2000)	Significance
Lead	0.5-20	57	40	1.4	1-2	slight pollution
Cadmium	0.5-20	2.26	0.5	4.5	4-8	Sever pollution
Zinc	0.5-30	859.14	300	2.86	2-4	moderate pollution
Copper	0.5-20	337	500	0.6	0.51-0.75	Sever contamination

Table 3: Metal pollution index for soil sample at 30 meters distance from the periphery of Teppi town solid waste dump site.

Heavy metal	Depth (cm)	Site 30m	EEPA (mg/kg)	MPI	Class interval	Significance
Lead	15-30	52	40	1.3	1-2	slight pollution
Cadmium	15-30	1.26	0.5	2.38	2-4	moderate pollution
copper	15-30	286.11	500	0.57	00.51-0.75	Severe contamination
Zinc	15-30	826.45	300	2.75	2-4	Moderate pollution

Table 4 Metal pollution index for soil sample at 60 meters distance from the periphery of Teppi town solid waste dump site.

Heavy metal	Depth (cm)	Site 60m	EEPA	MPI	Class interval	Significance
Lead	15-30	3.26	40	0.08	<0.1	Very slight contamination
Cadmium	15-30	0.53	0.5	1.0.6	1-2	Slight pollution
copper	15-30	204.06	500	0.4	0.26-0.5	Moderate contamination
Zinc	15-30	623.3	300	5.4	4-8	Severe pollution

5.3. Physico-chemical parameters of the Surface Water and Leachate Samples

Table 5: The physico-chemical properties of stream water and leachate samples at Teppi town solid dump site along different sample location and guideline values.

Sample sites, mean values ± standard deviation of physico-chemical parameters with guideline values.

parameters	US	L	DS1	DS2	EEPA Standard	WHO Standard
Temperature (C°)	22±0.1	32.9±0.29	27.5±0.2	27±0.5	5-30	NA
pH	7.6±0.21	8.5±0.12	8.1±0.12	8.0±0.1	6-9	6.5-8.5
EC (µS/cm)	238.2±0.2	391.3±0.01	281.3±0.01	247.8±0.02	1000	1400
TDS (mg/l)	446.3±0.2	782.5±0.15	557.9±0.1	495.7±0.1	NA	500
Turbidity (NTU)	61.6±0.01	798.4±0.5	144.0±0.3	135.3±0.7	NA	25
Nitrate (mg/l)	0.8±0.01	1.88±0.01	1.72±0.01	1.48±0.01	50	30
Sulfate (mg/l)	16±0.1	98±0.09	26±0.8	63±0.5	200	200
Potassium (mg/l)	8.5±0. 05	20.1±0.29	12.1±0.17	9.8±0.15	NA	12
Fluoride (mg/l)	0.40±0.01	1.71±0.01	0.88±0.01	0.8±0.01	1	1.5
BOD (mg/l)	7.9	620.2	31	12	<5	<5
COD (mg/l)	10.51	935.33	61.33	18.4	5	<5

The above table 5 shows the mean values of temperature in the study area were revealed between 22.00±0.1°C and 32.9±0.029°C. The lowest water mean temperature was observed in the upper stream (22.00±0.1 °C). The mean values of pH in most of the water samples were slightly alkaline. The upper stream site was recorded the minimum pH value (7.6±0.21) with the leachate sample site was showed the maximum mean value of pH 8.5±0.11 and at P-value < 0.05 the means were significantly different.

Total dissolved solids indicate the salinity behavior of water. Water containing more than 500 mg/l of TDS is not considered desirable for domestic purpose and drinking water supplies WHO (2004). Table 5 shows the mean value of TDS in the study area varied from 476.3±0.26 mg/l to 782.5±0.15 mg/l; moreover, the means were significantly different at p-value < 0.05 level. In most water turbidity is due to colloidal and extremely fine dispersions. The mean turbidity values were varied between 61.6±0.01 and 798±0.5 NTU.

The sample point of leachate was higher values of turbidity recorded 798±0.5 NTU. The other sites such as near to dump site and the downstream were measured 144±0.3 and 135±0.7 NTU respectively. The conductivity in water sample showed a high increment in leachate sample recorded 391.35±0.01 and the minimum value of EC was measured in the upper stream which showed 238.2±0.2 µS/cm and the means were significantly different at p-value < 0.05 level.

5.4. Biological and Chemical Parameters of the Surface Water and Leachate Samples

Table 5 shows BOD_5 result for the water samples ranged from a minimum of 7.9 mg/l in the upper stream up to a maximum of 31 mg/l at near to dump site except for the leachate sample the highest BOD_5 value was revealed 620 mg/l. The results of COD in the study area were 10.51 mg/l, 935.3 mg/l, 61.33 mg/l and 18.4 mg/l in upper stream, leachate, near to dump site and downstream respectively. The amount of nitrate in the study area was measured between 0.8±0.01 and 1.88±0.01 mg/l. The finding were varied from the upper stream which recorded the lowest value compared to the other sample sites even if it was higher than the natural background level of 0.23 mg/l. The remaining sample sites such as leachate, near to dump site and downstream were recorded 1.88±0.01, 1.72±0.01 and 1.48±0.01 mg/l respectively and at P-value < 0.05 the means were significantly different.

In the present analysis, fluoride concentration was found in all samples sites. The maximum concentration was found to be 1.71±0.01 mg/l in leachate sample and the minimum mean value was measured in the upper stream (0.4±0.01mg/l) and the means were significantly different at p-value < 0.05 level. The above table 5 shows that the mean values of sulfate in the study area were between 16±0.17 mg/l and 98±0.09 mg/l. The highest mean value was registered in leachate and downstream sample sites 98±0.09 and 63±0.5 mg/l respectively and the upper stream was recorded the lowest mean

value (16±0.2 mg/l). In addition, at P-value < 0.05 the means were significantly different. The mean value of potassium in leachate site was higher (20±0.29 mg/l), whereas the mean value of potassium in upper stream sample site was recorded 8.5±0.05± mg/l lower than the sample sites near to dump site and downstream were revealed 12.±0.17mg/l, 9.7±0.15mg/l respectively and at P-value < 0.05 the means were significantly different.

5.5. Heavy Metal Result of Stream water and Leachate samples

Table 6: Concentration of Cd, Cu, Pb, Zn, Ni and Mn in stream water and leachate samples at Teppi town solid dump site along sample locations with different guideline values.

Sample sites, mean values± standard deviation with guideline values.						
Parameters	US	L	DS1	DS2	EEPA Standard	WHO Standard
Cadmium (mg/l)	Bdl	0.3±0.01	Bdl	Bdl	0.005	0.003
Copper (mg/l)	Bdl	0.26±1.084	0.02±0.95	0.018±1.04	0.05-1.1	2
Lead (mg/l)	Bdl	0.08±0.1	Bdl	Bdl	0.1	0.05
Zinc (mg/l)	0.211±0.2	0.54±0.2	0.39±0.18	0.34±0.2	0.5	0.05
Nickel (mg/l)	Bdl	0.4±0.1	0.08±0.1	0.06±0.13	0.1	0.02
Manganese (mg/l)	0.18±0.01	0.66±0.04	0.4±0.1	0.22±0.1	0.3	0.1

The above table 6 shows the concentration of cadmium in all water samples were below detection limit (< 0.02 mg/l) except for the leachate sample was recorded 0.3±0.01mg/l. A concentration of copper in water samples was found to be 0.26±0.9, 0.02±0.95, and 0.018±1.04 in leachate, near to dump site, and downstream respectively and at P<0.05 the means were significantly different. The lowest concentration was revealed in the upper stream below the detection limit (<0.018mg/l). A concentration of zinc in water samples were 0.21±0.2, 0.54±0.2, 0.39±0.18, and 0.34± 0.2 mg/l in

upper stream, leachate, near to dump site, and downstream respectively and at P- value < 0.05 the means were significantly different.

The above table 6 shows that nickel concentration was high in most of the samples and its peak value was detected in the leachate sample (0.4±0.13mg/l) and the lowest concentration of nickel was observed in the upper stream revealed below the detection limit (< 0.04 mg/l) and at P-value < 0.05 the means were significantly different. The above table 3 shows that the mean values of lead were below the detection limit (<0.08mg/l) in the upper stream, near to dump site and downstream sample sites. However, the leachate sample site was recorded 0.08±0.1 mg/l. The mean values of manganese in the study area were 0.18±0.01 mg/l in the upper stream, 0.66±0.04 mg/l in leachate, 0.4±0.01 mg/l in near to dump site and 0.22±0.01 mg/l in downstream. However, the means were not significantly different at p-value < 0.05 level.

CHAPTER SIX

6. DISCUSSION

6.1. Soil pH and EC

Soil pH is very important for most heavy metals since metal availability is relatively low when pH is around 6.5 to 7. Lower pH would favor availability, mobility, and redistribution of the metals in the various fractions (Aydinalp and Marinova, 2003; Haberhauer, 2007; Adelekan and Alawode, 2011; Abdourahamane *et al.*, 2015) and increasing soil pH increases cationic heavy metal retention to soil surfaces via adsorption, inner sphere surface complexation, and/or precipitation. In addition, heavy metal mobility decreases with increasing soil pH (8 and above) due to precipitation of hydroxides and formation of insoluble organic complexes (Appel and Ma, 2002; Jiang *et al.*, 2012; Akan *et al.*, 2013; Shiva Kumar and Srikantaswamy, 2014).

Soil pH in all sample sites was recorded slightly basic. Similar studies conduct in Addis Ababa, Accra (Ghana), Lagos (Nigeria), Maradi city (Niger Republic), and Adama (Ethiopia) solid waste disposal sites show slightly basic pH between 8.17 and 7.37 in the nearby dump sites. It might be due to a soil with the high metallic burden (Beyene and Banerjee, 2011; Osei *et al*., 2011; Adedosu *et al.*, 2013; Abdourahamane *et al.*, 2015; Kebede *et al.*, 2016).

The EC values of soil at Teppi town solid waste dump site indicate the significant presence of trace metal ions or ionizable materials in the soil (Anapuwa and Precious, 2015). Therefore, the sample site 60 meters far from the dump site was recorded the lower EC values may show the low trace metal ions or ionizable materials presence in the soil compared to the other sample site. However, the mean values of EC found in this study were less compared to another similar study at Addis Ababa dump site (Beyene and Banerjee, 2011) and the difference may be due to the composition of the waste and the soil condition.

6.2. Heavy Metals in Soil Samples

Heavy metals are inorganic elements essential for plant growth in traces or very minute quantities. They are toxic and poisonous in relatively higher concentrations (Aderinola *et al.*, 2009; Jayanthi.M, 2014). Two factors contribute to the deleterious effects of heavy metals as environmental pollutants. Firstly, they cannot be destroyed through biological degradation as in the case of most organic pollutants. Secondly, they are easily assimilated and can bioaccumulate in the protoplasm of aquatic organisms (Wuana *et al.*, 2010; Wogu and Okaka, 2011). In light of this fact, the following trace elements were measured in the soil.

Lead is not an essential element. It is well-known to be toxic and can cause serious injury to the brain, nervous system, red blood cells, and kidneys. Exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. In general, plants do not absorb or accumulate lead. However, on soils testing high in lead, it is possible for some lead to be taken up and it can accumulate in individual organisms, but also in entire food chains (Wuana and Okieimen, 2011; Nartey *et al*., 2012).

The highest mean values of lead were observed in 10 meters and 30 meters far away from dump site recorded 57.56±0.26 and 52.12±0.02 mg/kg respectively and the values were higher than the limit prescribed by EEPA (2003) standard (40 mg/kg). The movement of lead along the distance was favored by slight nearest to the periphery of the dump site. It may be due to differences in soil pH and organic matter.

According to Dube *et al.* (2001), Barancikova and Makovnikova (2003), Bradl (2004), Yang *et al.* (2006), Fern *et al.* (2007), Haberhauer (2007), Ashworth and Alloway (2008), and Shiva Kumar and Srikantaswamy (2014), it might be due to the presence of clay particle and organic matter. They are the major contributors towards sorbing of heavy metals. In addition, organic matter is important for the retention of metals by soil solids, thus decreasing mobility and bioavailability. The soil texture contributes a positive role in the mobility of metals in the soil profile. The soil consists of fine particles and clays. These particles and clays are most important and act as adsorption/binding surface of heavy metals in soils.

Kebede *et al*. (2016) and Ideriah *et al*. (2010) also substantiate this finding along the distance; however, the concentration was different compared to these study areas. This can be due to adsorption of lead on decomposed organic in sample sites near to dump site that restricts its mobility. In addition, it might be due to differences in the composition of the waste and the age of dump sites. However, the values of lead in this study area was lower compared to other studies done in Addis Ababa, India, and Maradi city (Niger Republic) dump sites which shows 17-852 mg/kg, 42.9-1833.5 mg/kg, and 79.133 mg/kg respectively (Beyene and Banerjee, 2011; Abdourahamane *et al.,* 2015). It was higher than another study conducted by Kebede *et al*. (2016) in Adama city (Ethiopia) dump site which shows 1.033 mg/kg. The difference may be due to the quantity and constitute of municipal solid waste that contains lead contents such as electronic waste, lead batteries, lead-based paints, pipes, plastics were indiscriminately dumped in the dump sites.

Cadmium is one of the most toxic heavy metals in the arable soil for crop growth and yield formation. It originates mainly from anthropogenic activities such as industrial processes, mining activities and disposal of cadmium-containing solid waste, sewage sludge, and phosphate fertilizers. Plants may absorb cadmium from soil and irrigation water. Once in the plants, cadmium may become a part of food chain and cause harmful effects on human health (Huang *et al.*, 2009; Maqbool *et al*., 2011).

Cadmium is readily accumulated by many organisms, particularly by microorganisms and mollusk. Soil invertebrates also concentrate cadmium markedly. Chronic exposure to the metal produces a wide variety of acute and chronic effects in mammals similar to those seen in humans. Kidney damage and lung emphysema are the primary effects of high cadmium in the body (Nartey *et al*, 2012). Cadmium is known to inhibit bone repair mechanisms and is teratogenic, mutagenic and carcinogenic effects (EEPA, 2003).

Its values also revealed in all along the distance in sample stations with the lowest value was measured in the 60 meters far from the dump site and the highest value was recorded in 10 meters distance from the dump site showed 2.26±0.21 mg/kg. According to Dube *et al.* (2001), Aydinalp and Marinova (2003), Bradl (2004), Fern *et al.* (2007), Haberhauer (2007), Ashworth and Alloway (2008), and Abu-Zahra *et al.* (2010) the highest concentrations with distance variation may be related with sorption of metals into a nature of soil with organic matter and pH. Thus, it was expected to find different concentration in the 10 meters and 30 meters far away from the periphery of the dump site.

The values of cadmium in10 meters, 30 meters, and 60 meters away from the dump site were higher than the limit prescribed by EEPA (2003) standard (0.5 mg/kg). In addition, 10 meters and 30 meters away from the dump site were revealed higher values than the limit value prescribed by US EPA standard (1.4 mg/kg). Different international authors fix a normal cadmium range of 0.07 and 1.1 mg/kg (Alloway, 1990; Kabata and Pendias, 2001). Concentrations above 0.5 mg/kg could reflect the influence of human activity (Mico *et al.*, 2006).

The finding was substantiated by other studies conducted in Adama and Addis Ababa solid waste dump sites reveal the higher average content of cadmium at nearest to the dump site (Beyene and Banerjee, 2011; Kebede *et al*., 2016). This indicated that solid waste open dump site contributes to increasing the concentration of heavy metals in the nearest soil. The finding in this study was higher than the findings of Abdourahamane *et al.* (2015) and Kebede *et al*. (2016) in Maradi (Niger Republic) and Adama (Ethiopia) dump sites respectively. However, The finding in this study was lower than another finding of Beyene and Banerjee (2011) in Addis Ababa dump site. The reason might be due to the difference in the age of dump sites and type of cadmium-containing wastes such as paints, batteries, plastics, agricultural use of sludge, fertilizers, galvanized materials, and cadmium-plated containers were indiscriminately disposed of in the dump sites.

Copper is an essential micro-nutrient required for the growth of both plants and animals. In humans, it helps in the production of blood hemoglobin. In plants, copper is especially important in seed production, disease resistance, and regulation of water. Copper is indeed essential, but in high doses, it can cause anemia, liver and kidney damage, stomach and intestinal irritation (Wuana and Okieimen, 2011). The normal copper content of agricultural soils is 5 to 50 mg/kg. Concentrations below 8 mg/kg could indicate deficiency for some crops as copper is an essential micro-nutrient (Mico *et al.*, 2006).

The highest concentrations with distance variation may be due to differences in soil pH and organic matter. The values of copper in the study area was higher than the finding of Prechthai *et al.* (2008), Ideriah *et al.* (2010) and Beyene and Banerjee (2011). Moreover, the values were higher than the limit prescribed by US EPA standard of 200 mg/kg Haliru *et al.* (2014) except for the reference site. However, the values of copper in the study area were lower than the limit value prescribed by EEPA (2003) standard of 500 mg/kg.

Zinc is a 'masculine' element that balances copper in the body and is essential for male reproductive activity. However, the excess amount can cause system dysfunctions that result in impairment of growth and reproduction. In addition, zinc can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms, thus retarding the breakdown of organic matter (Duruibe *et al*, 2007; Wuana and Okieimen, 2011). Zinc occurs naturally in soil (about 70 mg/kg in crustal rocks) but zinc concentrations are rising unnaturally due to anthropogenic additions (Wuana and Okieimen, 2011).

The highest concentrations with distance variation may be related with adsorption of metals into a nature of soil with organic matter, texture, and pH (Dube *et al.*, 2001; Bradl, 2004; Fern *et al.*, 2007; Haberhauer, 2007; Abu-Zahra *et al.*, 2010; Shiva Kumar and Srikantaswamy, 2014). The values of zinc in the study area was higher than the finding of Beyene and Banerjee (2011) and Abdourahamane *et al,* (2015) in Addis Ababa (Ethiopia) and Maradi city (Niger Republic) dump sites shows 131.8 mg/kg and 97.98 mg/kg respectively. It might be due to discharges of smelter slag, wastes, and the use of commercial products such as fertilizers and wood preservatives that contain zinc disposed of in the dump sites.

Zinc demonstrated considerable high mean values in the sample sites unless the reference one. It indicating that soil where largely polluted with zinc around the solid waste dump site. According to Haliru *et al.* (2014), it was revealed higher values than normal concentration in soil. Additionally, it was higher values than the limits prescribed by EEPA, US EPA, EU and UK guideline values between 150 and 300 mg/kg.

6.2.1. Metal pollution Index for soil samples

The above table 3, 4 and 5 shows MPI values of lead at 10 meters and 30 meters sample sites were demonstrated excessive up to severe pollution and 60 meters away from the dump site revealed slight pollution of lead than the reference sites. Similarly, MPI values of copper in all sample sites were illustrated slight pollution than reference site. MPI values of cadmium in all sample sites were revealed severe pollution than the reference site. In addition, MPI values of zinc in all sample sites were confirmed severe pollution than the reference site.

Generally among analyzed parameters pH was slightly basic. Besides EC was lower in 60 meters far from the dump site and higher in the 10 and 30 meters sample sites which indicate the presence of trace metal ions due to the influence of solid waste dumped in the nearby soil. The values of lead, copper, cadmium, and zinc were varied along the distance in all location which is an indicator for sorption of heavy metals into the soil organic matter, pH, and composition of waste in different part of the dump site affect the value of these heavy metal concentrations varied in sample locations.

The result of heavy metals in soil such as lead, cadmium, zinc, and copper of reference site was lower than other sample sites were revealed slight pollution up to severe pollution. Zinc, cadmium, and copper results were above the limit value prescribed by US EPA standards. In addition, lead, cadmium, and zinc were also above the limit value prescribed by EEPA (2003) standard. It indicates the open dump approach of a solid waste disposal system in Teppi town has been altering soil quality near to the dump site and probable source of human health risk via the food chain. This might be due to indiscriminate disposal of solid waste and erosion of leachate during the high rainy season.

6.3. Physico-chemical and biological parameters of surface water and leachate samples

Temperature affect microbial growth among other characteristics of water and it is also a known fact that the rate at which chemical reactions occur increase with increasing temperature and the rate of biochemical reactions usually double for every $10.0°_C$ rise in temperature. Physically, less oxygen can dissolve in warm water than in cold water (Nartey *et al*., 2012). Cool water is generally more palatable than warm water and temperature will impact on the acceptability of a number of other inorganic constituents and chemical contaminants that may affect taste. High water temperature enables the growth of microorganisms and may increase taste, odor, color and corrosion problems WHO (2004). This is because increased temperature decreases the solubility of gases in water. It is for these reasons that the temperatures of the water samples were determined for the river systems.

A study increase in water temperature in the course of leachate, downstream and the point near to dump sites were noticed i.e. 32.00±0.02°C, 27.00±0.2°C, and 27.00±0.5°C respectively. A high in temperature was observed from leachate up to downstream. This might be due to differences in altitude and the presence of the effluents emanated from the open dump site. Since water temperature affects the concentration of biological, physical, and chemical constituents of water, the relatively high

temperatures recorded would speed up the decomposition of organic matter in the water (Nartey *et al.*, 2012).

The leachate sample was recorded higher pH (8.5±0.11). This shows that the leachate was alkaline and this was typical of sample from aged wastes (Osei et al., 2011) and near to dump site and downstream sample sites recorded 8.1±0.11 and 8±0.1 respectively. The higher range of pH indicates higher productivity of water. Another studies conducted by Nkowacha *et al.* (2011), Karijia *et al.* (2013), Nirmala Dharmarathne (2013) and Hailemariam and Ajeme (2014) in Nigeria, Juba (South Sudan), Sri Lanka, and Addis Ababa (Ethiopia) solid waste dump sites respectively substantiate this finding which shows slightly basic pH in the nearby stream. However, the mean values of pH of water samples varied between 7.6±0.21 and 8.5±0.1were found the limit value prescribed by World Health Organization (2004) between 6.5 and 8.5 and limit value prescribed by EEPA (2003) between 6 and 9.

The mean value of TDS in sample point of the upper stream, leachate, near to dump site, and downstream from the dump sites were registered 446.3±0.26, 782.5±0.15, 557.9±0.1, and 495.7±0.1mg/l respectively. The sample points of leachate and near to dump sites were showed higher TDS values than the limit prescribed by WHO (2004) standard (500 mg/l). On the other hand sample point of the upper stream was lower values of TDS. This might be due to the effect of the dump site.

The lowest mean value of turbidity was observed in the upper stream sample site 61.6±0.01 NTU even though it was above the limit prescribed by WHO (2004) standard value (25 NTU). It might be due to indiscriminate disposal of waste into the water bodies. The higher turbidity in the other sites might be due to the influence of open dump site. It was the highest turbidity values than investigated by Gopalkrushna (2011) in and around Akoyo city and Aljaradin and Persson (2012) in Jordan dump sites are reveal between 13.4 and 4.7 NTU and between 40 and 160 NTU respectively in the nearby stream and leachate water.

According to the US EPA (2002) turbidity values between 0.0 and 5.0 NTU show no visible turbidity, no adverse aesthetic effects and no significant risk of infectious disease transmission. The values 10 NTU have severe aesthetic effects and the water carries an associated risk of diseases due to infectious agents and chemicals absorbed onto particulate matter (Nartey *et al.*, 2012).

Electrical conductivity (EC) is a measure of water capacity to convey electric current. It signifies the amount of total dissolved salts (Gopalkrushna, 2011) and it is also defined as a number of ions

(positive and negative) offer in water (Hasan *et al.*, 2016). The sample site of leachate, near to dump site, and downstream sample sites were recorded the maximum EC values than the upper stream. However, they fell under the EEPA (2003) and WHO (2004) acceptable limits of 1000 and 1400 µS/cm respectively.

High EC value was observed in leachate sample 391.35 µS/cm. It indicating the presence of high amount of dissolved inorganic substances in ionized form in and around solid waste dump site (Siddiqui, 2015). In addition, the higher value of EC is a good indicator of the presence of contaminants such as potassium and sulfate (Nazir *et al.*, 2015).

When considering the average value of conductivity in leachate sample concluded that leachate was the high amount of ionizable material. The result of this study was less than the other studies conducted in Addis Ababa (Ethiopia) and Sri Lanka solid waste dump sites show 1102 µS/cm up to 3720 µS/cm and 1136 µS/cm respectively in the nearby stream (A.Abiye, 2012; Dharmarathne and Gunatilake, 2013). The result of this study was higher than a similar study conducted in Juba (South Sudan) the average values of electrical conductivity show between 89µS/cm and 229µS/cm in the nearby stream (Karijia *et al.*, 2013).

According to EU guidelines, the COD value in drinking water is 5 mg/l (Maqbool *et al.*, 2011). Figure 18 indicates the results of COD values of sample sites recorded during the study period. It was observed that the values were higher than the permissible limit in all samples. It indicates the stream water was highly polluted with the chemicals which might have resulted from the solid waste dump site and indiscriminate disposal of solid waste in the nearby stream.

Nitrogen which usually exists in water bodies as nitrate is a key ingredient in fertilizers. It generally becomes a pollutant in saltwater or brackish estuarine systems where nitrogen is a limiting nutrient. Surplus amounts of bioavailable nitrogen in marine systems lead to eutrophication and algae blooms (Nartey *et al*., 2012).

Nitrate values in all the sites were registered higher than the natural background level of 0.23 mg/l. The presence of nitrate may be the result of waste being disposed of at the dump sites and indiscriminate disposal of solid waste into the water body. Thus, contamination of the water bodies with chemicals from the dump sites is likely to occur. It could be attributed to runoff from farms along

the banks of the rivers which may contain organic fertilizers. The values of nitrate in the study area were lower than the similar studies conducted in Addis Ababa (Ethiopia) and Accra (Ghana) solid waste dump sites shows nitrate concentration between 2.0-2.2 mg/l and 4.18-30.8 mg/l respectively in the nearby stream (A.Abiye, 2012; Nartey *et al.* (2012) and higher than another study conducted at Accra (Ghana) nitrate concentration reveal 0.046 mg/l in the upper stream up to 0.418 mg/l in the downstream (Osei *et al.*, 2011).

Nitrates are the most common form of nitrogen found in natural waters with enough dissolved oxygen. The natural background levels of nitrate may come from rocks, land drainage, plant and animal matter. An extremely high concentration of nitrate is toxic (Nartey *et al.*, 2012). However, the values revealed for all the sample sites did not exceed the limits prescribed by WHO (2004) and EEPA (2003) standards of 20 mg/l and 50 mg/l respectively.

The probable source of high fluoride in waters seems to be that during weathering and circulation of water in rocks and soils. Fluorine is leached out and dissolved in groundwater. Excess intake of fluoride through drinking water causes fluorosis on the human being (Gopalkrushna*, 2011)*.

All sample sites were recorded under the limit prescribed by EEPA (2003) 1 mg/l and WHO (2004) guideline value of 1.5 mg/l except for the leachate (L) sample site the mean value was measured 1.71±0.01 mg/l. However, the remaining site especially the point near to dump site (DS1) and the downstream sample location (DS2) registered the highest concentration compared with the upper stream (0.8±0.01mg/l). It was the highest result compared with Gopalkrushna (2011) finding lie less than 0.05mg/l in the nearby stream. This might be due to fluoride-containing materials such as wood preservatives, glasses, and enamel indiscriminately dumps in an open dump site and in the nearby stream.

Sulfate occurs naturally in water as a result of leaching from gypsum and other common minerals. Discharge of domestic wastes tends to increase its concentration (Gopalkrushna, 2011).

All mean values of sulfate were below the limits prescribed by EEPA (2003) and WHO (2004) standards (200 mg/l). The values were lower than other findings in Akot city and Addis Ababa solid waste dump sites the sulfate concentration varies between 263-62.8 mg/l and 53-342 mg/l respectively (Gopalkrushna, 2011; A.Abiye, 2012) in the nearby stream but the values were higher than another

finding in Accra (Ghana) dump site shows sulfate concentration varies b/n 0.2 mg/l in upper stream and 25 mg/l in leachate water (Osei *et al.*, 2011).

The major source of potassium in natural freshwater is weathering of rocks but the quantities increase in the polluted water due to the disposal of waste in the water body *(Gopalkrushna, 2011)*. The potassium concentration in water samples was lower than 73 mg/l investigated by Kamboj *et al.*, (2013) and potassium concentration in the study area was higher than 15 mg/l to 5.1 mg/l investigated by Gopalkrushna (2011).

Biochemical Oxygen Demand (BOD) is used as an index for determining the amount of decomposing organic materials as well as the rate of biological activities in the water. This is because oxygen is required for respiration by microorganisms involved in the decomposition of organic materials. This high concentration of BOD indicates the presence of organic effluent and hence oxygen-requiring microorganisms (Nartey *et al*., 2012).

The values of BOD_5 in the study area were higher than the limits prescribed by EEPA (2003) and WHO (2004) standards of 5 mg/l. In addition, it was higher than a similar study conducted in Accra (Ghana) reveal 1.25 mg/l up to 100 mg/l in the nearby stream and leachate samples respectively (Osei *et al.*, 2011). The high BOD_5 values may be attributed to the discharge of organic waste into water bodies resulting in the uptake of DO in the oxidative breakdown of these wastes (Tamiru.A, 2001). The dump site was a factor promoting the loading of the water body with organic matter hence, the high BOD_5 value.

The implication of high BOD_5 in surface water could also mean that the oxygen present in the water will be used for decomposition of the pollutants and not available for aquatic life anymore. The natural background level of fresh water ranges from 1.0 to 3.0 mg/l. The BOD of a river must generally not exceed 4.0 mg/l. This would reduce DO from saturating to 5.0 - 6.0 mg/l which is still capable of supporting aquatic life (Nartey *et al.*, 2012).

6.4. Heavy Metals in River Water and Leachate Samples

Indiscriminately dumping of solid wastes in open dump sites exposes the metals to air and rain thereby drain to water bodies. When agricultural soils are polluted these metals are taken up by plants and consequently accumulate in their tissues. Animals that graze on such contaminated plants and drink

from polluted waters as well as marine lives that breed in heavy metal polluted waters also accumulate such metals in their tissues and milk. Humans are in turn exposed to heavy metals by consuming contaminated plants and animals and this has been known to result in various biochemical disorders. Finally, living organisms within a given ecosystem are variously contaminated along their cycles of the food chain. In light of these facts, the following heavy metals were assessed in stream water near to Teppi town solid waste dump site.

Cadmium is toxic at extremely low levels. In humans, long-term exposure results in renal dysfunction. High exposure can direct to obstructive lung disease, cadmium pneumonitis, resulting from inhaled dust and fumes. It is characterized by chest pain, cough with foamy, bloody sputum, and death of the lining of the lung tissues because of excessive accumulation of watery fluids. Cadmium is also related with bone defects (Duruibe *et al.*, 2007).

Table 4 shows that the concentration of cadmium in all water samples were below detection limit (<0.02mg/l) and below the limit prescribed by EEPA (2003) and WHO (2004) standards 0.005 and 0.003 mg/l respectively except for leachate sample was revealed 0.3±0.01mg/l. It might be due to the solid waste composition that contained batteries and paints were indiscriminately disposed of in the dump site. It also might be due to the organic matter, pH, and texture of soil (Dube *et al.*, 2001; Bradl, 2004; Fern *et al.*, 2007; Haberhauer, 2007; **Abu-Zahra** *et al.*, 2010; Shiva Kumar and Srikantaswamy, 2014) near to dump site which adsorbed the heavy metal and retained on it. Other studies in Accra (Ghana) and India confirm this finding (Raman and Narayanan, 2008a; Osei *et al.*, 2011; Nartey *et al.*, 2012) cadmium concentration in surface water near to the dump site shows lower than 0.003 mg/l.

Copper is one of the world's most widely used metals. Although copper occurs naturally in most waters, it is regarded as potentially hazardous by the USEPA. The occurrence of natural sources of copper in the aquatic environment is due to weathering processes and disposal of municipal solid waste. Metallic copper is insoluble in water, but many copper salts are highly soluble as cupric or cuprous ions. Anthropogenic sources account for 33-60% of the total annual global input of copper to the aquatic environment (EEPA, 2003).

According to EEPA (2003), the water quality range for copper for which there is no health or aesthetic effect is between 0.05 mg/l and 0.11 mg/l and all the sites fell within this range except for the leachate

sample showed the highest value of copper was revealed above the limit prescribed by EEPA (2003) and WHO (2004) standards (0.1 mg/l).

It also higher value than similar studies conducted in Accra (Ghana) dump site reveal below 0.059 mg/l and lower than another finding in Sri Lanka the values of copper in surface and leachate water near to dump site reveal between 0.08 and 9.9 mg/l (Osei *et al.*, 2011; Nirmala Dharmarathne, 2013). Hence, copper levels in the river systems pose no threat to the environment and human health.

Zinc is one of the important trace elements that play a vital role in the physiological and metabolic process of many organisms. However, higher concentrations of zinc can be toxic to the organism. It plays an important role in protein synthesis and is a metal which shows fairly low concentration in surface water due to its restricted mobility from the place of rock weathering or from the natural sources.

The values of zinc in the study area were higher than another study conducted in Accra (Ghana) the concentration of zinc nearby stream is below detection limit (Nartey *et al.*, 2012), however, lower than another finding in Sri Lanka record 0.1-9.9 mg/l in leachate water (Nirmala Dharmarathne, 2013). It might be due to discharges of smelter slag and wastes, and the use of commercial products such as fertilizers and wood preservatives that contain zinc disposed of in the water body and in the nearby dump site. According to Maqbool *et al.*, (2011) the permissible limit of zinc in water is 0.05 mg/l save for consumer. According to EEPA (2003), the prescribed limit of zinc in surface water lies between 0.003 mg/l and 0.5 mg/l. However, the values of zinc in the study area revealed between the limit prescribed by EEPA (2003) except for the leachate sample exceeded the standard.

Nickel is an element that occurs in the environment only at very low levels and is essential in small doses, but it can be dangerous when the maximum tolerable amounts are exceeded. This can cause various kinds of cancer on different sites within the bodies of human and animals (Wuana and Okieimen, 2011).

According to WHO (2004), the standard value of a nickel is 0.02 mg/l. Nickel values at the site near to dump site (0.08mg/l) and the downstream locations (0.06 mg/l) were slightly greater than the permissible standard limit of WHO (2004) except for the upper stream the lowest concentration of nickel was observed below in detection limits (< 0.04 mg/l). However, the values were lower than the

limit prescribed by EEPA (2003) 0.1 mg/l except for the leachate sample. It might be due to indiscriminate disposal of nickel-containing solid wastes such as electroplating, zinc base casting and storage battery indiscriminately dump in open dump site near to the river. Another finding in Abbottabad (Pakistan) and Sri Lanka also authenticate this result nickel value ranges between 0.03 and 9.9 mg/l in the nearby stream and leachate water (Maqbool *et al.*, 2011; Nirmala Dharmarathne, 2013).

The leachate water had the highest lead concentration compared to other streams. In addition, it contained high lead value than the permissible limits of EEPA (2003) and WHO (2004) standard (0.05 mg/l). It might be due to quantity and constitute of municipal solid waste that contains lead contents such as electronic waste, lead batteries, lead-based paints, pipes, and plastics were indiscriminately disposed of in the dump site. Gradually, due to erosion leachate might drain into the stream and increase lead concentration in stream water. Other studies in India and Accra (Ghana) dump sites authenticate this finding (Raman and Narayanan, 2008; Nartey *et al.*, 2012) the lead values are revealed between below detection limit and 0.07mg/l respectively in the nearby surface water.

Manganese occurs in surface waters that are low in oxygen and often does so with iron. When oxidized in aerobic waters, the oxide builds up in distribution causing severe discoloration at concentrations is > 0.05 mg/l (Nartey *et al.,* 2012).

The values of manganese at leachate and downstream sample sites were higher than the guideline values of EEPA (2003) 0.3 mg/l and WHO (2004) 0.1 mg/l. The presence of manganese might be due to indiscriminate disposal of solid waste in the river and discharge from a leachate. In addition, a high amount of manganese may be due to waste containing dry cell batteries, paints, glasses, and ceramics were disposed of in the open dump site and pollution from manganese dioxide cells for which the town has no controlled methods of disposal. The metal may also come from other sources such as domestic wastewater and sewage sludge disposal. Leachate and downstream sites registered the amount above prescribe limits of EEPA (2003) and WHO (2004) standards. However, the finding was lower than another finding of Nirmala Dharmarathne (2013) in Sri Lanka reveal 2.7 mg/l in leachate water near to dump site.

CHAPTER SEVEN

7. CONCLUSION AND RECOMMENDATIONS

7.1. Conclusion

Among analyzed parameters pH of soil was higher (above 8 and basic) which indicates the influence of solid waste dumped in the area. Similarly, EC was lower in 60 meters and higher in 10 meters and 30 meters sample sites and the organic matter of the soil was decrease move towards form the dump site. The concentration of heavy metals such as cadmium, zinc, lead, and copper in soils has been found to be higher than EEPA and USEPA standards. The leachate sample was recorded higher concentration of heavy metals content such as lead, cadmium, manganese, nickel, copper, and adding increased concentrations of heavy metals such as manganese, nickel, copper, and zinc, to the adjacent river water especially near to dump site and downstream compared with the upper stream of the river from the dump site.

Therefore, it can be presumed that uninterrupted disposal of all categories of solid waste on open land site resulted in the degraded quality of the soil and the surface water, gradually release of concentrated leachate to the soil and surface water which further becomes a latent source of entry into the food chain. The parameters exceeding the permissible limits of EEPA and WHO standards included pH, TDS, Turbidity, BOD_5, COD, manganese, and nickel. Consequently, the water of the stream has been polluted physically and chemically through the indiscriminate disposal of solid waste and discharge of leachate. Improper management of solid waste and the dump site may pose a serious health threat to communities utilizing the waters stream for drinking, irrigation, bathing, and other domestic purposes.

The sources of these pollutants into these water bodies were through runoffs from the municipal solid waste dump site and could also be attributed to indiscriminate and refuse disposal of solid waste which had contributed to elevated levels of the pollutants. The upper stream was low pollution status than other. This indicates pollution effect is more dependent on the location and distance from the dump site. Finally, the results indicated that the solid waste dump site has a pollution effect on surrounding soil and surface water quality in Teppi town.

7.2. Recommendations

In the short-term:

The municipality should pay attention to the present dumpsite should be left and treated accordingly to minimize the impact of persistent heavy metals in the soil to be used for further economical use of the land.

Research work should be carried out for selection of appropriate solid wastes dump site.

The soil in the study area needs different remediation technologies like Phytoremediation (use of plants for environmental cleanup) by growing certain plants in the area to minimize the rate of pollution and extent of future pollution problems.

The municipality should pay attention to prevent pollution of river water through construction of erosion preventive brim in order to control the discharge of leachate.

Constructions of geo-synthetic layer should be needed to prevent percolation of leachate into the groundwater.

The municipality should sensitize the population to reduce the quantity of waste produced through re-use and recycling of waste material.

In the long-term:

The Teppi town municipality should construct sanitary landfill to replace the present nearly indiscriminate disposal of solid waste in the open land, so as to reduce its level of nuisance on its immediate environment.

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Appendices

Table 7: Soil data description Mean standard deviation and p- value

parameters	10m Mean	SD	P value	30m Mean	SD	P value	60m Mean	SD	P value
pH	8.7	0.1	0.00032	8.4	0.1	0.00001	8	8.1	00000.1
EC	4920	1.04	0.00001	3490	0.66	0.0000	1800	0.5	0.0000
Lead	57.56	0.26	0.00001	52.21	0.02	0.00001	3.26	0.25	0.00001
Cadmium	2.26	0.2	0.000045	1.6	0.01	0.000045	0.53	0.01	0.000045
Copper	337.11	0.05	0.0000	286.11	0.2	0.000002	204.06	0.05	0.00002
Zinc	859.41	0.2	0.0000	826.45	0.01	0.0000	623.93	0.29	0.0000

SD= Standard Deviation

Table 8: Soil data with standard

Soil sample site	PH	Electrical conductivity	Organic matter	Lead(mg/kg)	Copper (mg/kg)	Cadmium (Mg/kg)	Zinc(Mg/kg)
10m	8.7±0.11	4920±1.04	4.67%OC× 1.724= 8.05%SOM	57.56±0.26	337.11±0.05	2.26±0.02	859.41±0.2
30m	8.4±0.1	3490±0.66	2.96%OC× 1.724+ 5.1%SOM	52.21±0.02	204.06±0.05	1.6±0.01	826.45±0.01
60m	8±0.1	1800±0.5	2.87%OC× 1.724= 4.95%SOM	3.26±0.25	286.12±0.2	0.53±0.01	623.93±0.29
US/EPA Standard	6.5-8.5	1400	NA	50-100	200	1.4	300
EEPA standard	6.5-9	1000	NA	40	500	0.5	500

The left side from± are mean values and the right sides from ± are the values of standard deviation; OC (Organic Carbon); SOM (Soil Organic Matter) and 1.724 (Conversion factor from % of OC to % of SOM)

NA= Not Available

Table 9: Water data description Mean value± standard deviation and P- value

Sample sites	Temperature	pH	EC	Turbidity	Fluoride	Sulfate	TDS	Potassium	Nitrate
US	22±0.1	7.6±0.21	238.2±0.2	61.6±0.01	0.40±0.01	16±0.1	446.3±0.2	8.5±0. 05	0.8±0.01
L	32.9±0.29	8.5±0.12	391.3±0.01	798.4±0.5	1.71±0.01	98±0.09	782.5±0.15	20.1±0.29	1.88±0.01
DS1	27.5±0.2	8.1±0.12	281.3±0.01	144.0±0.3	0.88±0.01	26±0.8	557.9±0.1	12.1±0.17	1.72±0.01
DS2	27±0.5	8.0±0.1	247.8±0.02	135.3±0.7	0.8±0.01	63±0.5	495.7±0.1	9.8±0.15	1.48±0.01
P Value	0.001	0.002	0.0005	0.002	0.000	0.0035	0.001	0.000	0.000

Table 10: mean value± standard deviation and p- value of water and leachate samples.

Sample sites	BOD mg/l	COD mg/l	Cadmium mg/l	Copper mg/l	Lead mg/l	Zinc mg/l	Nickel mg/l	Manganese mg/l
US	7.9	10.51	Bdl	Bdl	Bdl	0.211±0.2	Bdl	0.18±0.01
L	620	935.33	0.3±0.01	0.26±1.084	0.08±0.1	0.54±0.2	0.4±0.1	0.66±0.04
DS1	31	61.33	Bdl	0.02±0.95	Bdl	0.39±0.18	0.08±0.1	0.4±0.1
DS2	12	18.4	Bdl	0.018±1.04	Bdl	0.34±0.2	0.06±0.13	0.22±0.1
P value	--	--	0.000	0.00004	---	0.00031	0.000	0.09
WHO Standard	5	10	0.003	2	0.1	0.05	0.02	0.1
EEPA standard	<5	NA	0.005	0.05-0.11	0.05	0.5	0.1	0.3

The left side from± are mean values and the right sides from ± are the values of standard devotion

Bdl= (Below detection limit)   NA= Not Available

Annex

Annex 1. Reagents, apparatus and procedures used to analyzed of organic matter, EC and pH in the soil sample

Electrical Conductivity

➢ First prepared Potassium Chloride (KCl) 0.1 N solution through dried about 10g of KCl in the overnight at 105°C.

➢ The next day removed and cooled in desiccators.

➢ Weight exactly 7.45 g of the dried KCl and dissolved in distilled water in the 1-litre volumetric flask, bring to volume and mixed well.

➢ Weight 20g of soil samples into a 250ml beaker and added 50 ml of distilled water and shake on the automatic stirrer for 30 minutes.

➢ In 50 ml beaker, previously rinsed twice with the measured solution, pour 10ml of the 0.02 N KCl solutions and rinsed the cell of the conductivity meter, previously cleaned with distilled water with the 0.02 N KCl solutions.

➢ Then immersed the cell into the beaker containing the solution of 0.02 N KCl (USDA, 1982; Reeuwijk, 1992; Houba *et al.*, 1998)

➢ Measured the conductivity by digital EC meter (H12300 EC/TDS/NaCl meter, HAWA instrument, Romania, model).

Measuring pH in Water Suspension

➢ Weight 10g air dried < 2 mm soil sample into 100 ml beakers

➢ Added 25 ml distilled water from a measuring cylinder for 1:2.5 soil/water suspensions

➢ Transferred the samples to an automatic stirrer, stir for 30 minutes and measured pH on the upper part of the suspension.

➢ Then before effecting the following determination, rinse the electrode with a jet of water from a flash bottle and blot water droplets with tissue paper.

- Then read the soil pH in water after removed the samples from the automatic stirrer waited for about 1 minute for the soil particles to sediment and introduces the electrode into the suspension. Waited for 4 seconds before turning electrode knob from "check" to "auto"
- waited for the read to sterilized and recorded and the pH was measured using a pH meter (pH-016 model) (USDA, 1982; Reeuwijk, 1992; Houba *et al*., 1998).

Organic matter

Apparatus

- Erlenmeyer flask:500ml or 250ml
- Pipettes: (5 or 10 ml)
- Automatic Burette or Burette: 50ml
- Magnetic stirrer
- Dispenser
- Standard laboratory glassware
- analytical balance

Reagents

Use any reagent of recognized analytical grade and use distilled or ionized water for all solutions.

- Water, havening a specific conductivity not higher than 0.2 ms/m at 25 0c (grade 2 water in accordance with ISO 3696)
- Sulfuric acid, H_2SO4, concentrated (ρ=1.84g/cm3).
- Potassium chromate solution (k2Cr2O7*)* =1.62N*:* Dissolve 79.428g potassium chromate K2Cr2O7, in 1000ml volumetric flask and make up to the mark with water (volume to 1 liter)
- 0.5N Di-Ammonium Ferrous Sulphate (Mohr's Salt): Dissolve 392 g of Fe (NH4)2(SO4)2.6H_2O in distilled water. Add 20 ml of Conc.H_2SO4 and make up the volume to 2 liters with distilled water.

> Orthophosphoric acid: (85% and /or sodium fluoride, pure).

Barium Diphenylamine sulfonate indicator (1.6 %): Dissolve 1.6g barium diphenylamine

> Sulfonate in 100ml 98% H_2SO4.

WARNING: The chromate ion present in potassium dichromate is potentially toxic. Laboratory personnel working with this chemical standard should take appropriate precaution to avoid contact with, or ingestion of this chemical, following national or international safety regulation where applicable. Such regulations can extend to the disposal of solutions containing chromate ion, as these may also damage the environment. If in doubt, seek professional advice.

Laboratory Sample

Use the fraction of particle <2 mm of air dry soil sample pretreated in accordance with ISO 11464. Use part of the sample to determine the water content in accordance with ISO 11465. For the determination of carbon representative of sub sample of the laboratory sample should be milled until it passes a 250 μm aperture sieve in accordance with ISO 11464.

Procedures

The efficiency of the oxidation depends on the mass of the test portion, as well as the mass of carbon with in it, even if the potassium dichromate remains in excess. Experience has shown that, under the condition given in this international standard, the mass of carbon in the test portion should not exceed 20mg. Therefore; the mass of the test portion used should be in accordance with the table below.

Table 1: Mass of teats portion in relation with the estimated carbon content of the soil.

Estimated carbon content g/kg	0 to 40	40 to 80	80 to160	160 to 400	>400
Mass of the test portion mg	400 to 500	200 to 250	100 to 125	45 to 50	20 to 25

➢ Weigh 0.02-0.5 g air-dry soil sample in a 500/250ml conical flask. If soil contains too less carbon or too much carbon use the above table to set sample weight for analysis.

➢ Add 5ml of 1.62 N $K_2Cr_2O_7$ solutions and mix.

➢ Then, add 7.5 ml of concentration H_2SO_4 and swirl the flask 2 or 3 times gently while taking care not to take out to flask surface the sample.

➢ Allow the flask to stand for 30 minutes on an asbestos sheet for the reaction to complete. (Here, using heat insulator stand is recommended not to lose heat suddenly from the reaction mixture).

➢ Pour 100 ml of water to the flask to dilute the suspension. Filter, if it is expected that the end point of the titration will not be obvious.

➢ Add 10 ml of 85 % H_3PO_4 or 0.5g/ one spoon of the NaF and 1-2 ml of the Diphenylamine Sulfonate indicator and back- titrate the solution with 0.5 N Ferrous Ammonium Sulphate, till the color flashes from violet through blue to bright green.

➢ Register the volume of the Ferrous Ammonium Sulphate.

➢ Run a blank without sample simultaneously and QC sample or other controlling mechanism if available.

➢ Calculation and Expression of Result

Calculate percent of organic carbon (%OC), using the following equation:

$$\%OC = (B \quad A \times 0.39 \times N \times Mcf) \div S)$$

%of OM= %OC× 1.72

Where as

➢ 0.39 is calculation factor that obtained from: Meq of C=12/4=3→when converted to g it should be divided by 1000.

➢ 3/1000=0.003gm→when converted to % it multiplied by 100 0.003gm*100 = 0.3% when multiplied by 1.3 which means from 100 present carbon 77 oxidized by chromate.

0.3%*1.3= 0.39

Where:

B: Volume in ml of ferrous sulphate solution required for blank titration.

A: Volume in ml of ferrous sulphate solution required for sample titration.

0.39: Calculation factor

N: Normality of ferrous sulphate solution.

mcf: Moisture correction factor.

S: Weight of soil sample in gram

1.724: Conversion factor from % OC to % OM (Considering 58% of OM is OC)

Note: In this method about 77 percent of the C is oxidized by potassium dichromate, so a correction factor of 100/77 =1.3 is used in the calculation

Annex 2: Reagents, apparatus and procedures used for Heavy metal analysis

Water and leachate samples

Apparatus

➢ Hot plate
➢ Conical (Erlenmeyer) flasks, 125-ml, or Griffin beakers, 150-ml, acid-washed and rinsed with water
➢ Volumetric flasks, 100-ml.
➢ Watch glasses
➢ Steam bath

Reagent

➢ Nitric acid, HNO_3 concentration, analytical grade or better.
➢ Hydrochloric acid, HCl, concentration, analytical grade.
➢ Standard metal solutions: Prepare a series of standard metal solutions in the optimum concentration range by appropriate dilution of the following stock metal solutions with water containing 1.5 ml concentration. HNO_3/L. Prepare as described

below. Thoroughly dry reagents before use. In general, use reagents of the highest purity. For hydrates, use fresh reagents. Use pure metal stock solution if you have.

➤ Cadmium: Dissolve 0.100 g cadmium metal in 4 ml concentration. HNO_3. Add 8.0 ml concentration. HNO_3 and dilute to 1000 ml with water; 1.00 ml = 100 µg Cd.

➤ Copper: Dissolve 0.100 g copper metal in 2 ml concentration HNO_3 adds 10.0 ml concentration HNO_3 and dilute to 1000 ml with water; 1.00 ml = 100 µg Cu.

➤ Lead: Dissolve 0.1598 g lead nitrate, Pb $(NO_3)_2$, in a minimum amount of 1 + 1 HNO_3, add 10 ml concentration HNO_3, and dilute to 1000 ml with water; 1.00 ml = 100 µgPb.

➤ Manganese: Dissolve 0.1000 g manganese metal in 10 ml concentration of HCl mixed with 1 ml concentration HNO_3. Dilute to 1000 ml with water; 1.00 ml = 100 µgMn.

➤ Nickel: Dissolve 0.1000 g nickel metal in 10 ml hot concentrations HNO3, cool, and dilute to 1000 ml with water; 1.00 ml = 100 µg Ni.

➤ Zinc: Dissolve 0.100 g zinc metal in 20 ml 1 + 1 HCl and dilute to 1000 ml with water; 1.00 ml = 100 µg Zn.

Procedures

➤ Transfer a 100ml of well-mixed and acid-preserved sample appropriate for the expected metals concentrations to a flask or beaker.

➤ In a hood added 3 ml concentration of HNO_3 and covered with a ribbed watch glass.

➤ Placed flask or beaker on a hot plate and cautiously evaporate to less than 5 ml, making certain that sample did not boil and that no area of the bottom of the container was allowed to go dry.

➤ Cooled, rinsed down walls of the beaker and watch glass with a minimum of metal-free water and added 5 ml concentration of HNO_3.

➤ Then covered container with a no ribbed watch glass and returned to the hotplate.

➤ Increase the temperature of the hotplate so that a gentle reflux action occurred.

➤ Continue heating, added additional acid as necessary, until digestion was completed (generally indicated when the digest ate is light in color or does not change in appearance with continued refluxing).

➤ Cooled and added 10 ml 1 + 1 HCl and 15 ml water per 100 ml anticipated final volume.

➤ Then heat for additional 15 minutes to dissolve any precipitate and residue.

➤ Then cooled, washed down the beaker walls and watch glass with water, filtered to remove insoluble material and transferred filtrate into 100 ml volumetric flask with rinsing.

➤ Prepared the standard series of metal from the stock solution dilution with the same concentration of acid used to prepare a stock solution (Standard solution of each metal was prepared by dissolving 1.0 g of the metal in a minimum volume of 1:1 nitric acid. This was then diluted to 1liter to produce a1000 ppm solution). The detection limit of the instrument was listed below:

Copper 0.018- 4.0 mg/l

Cadmium 0.02- 2.20 mg/l

Manganese 0.01 - 3.5 mg/l

Lead 0.08- 14.0 mg/l

Nickel 0.04-8.0mg/l

Zinc 0.01- 3.0mg/l

Mg/l of metal =

$$\frac{(Concentration\ of\ Sample - Concentration\ of\ Blank)\ x\ Extraction\ Volume\ x\ DF}{Sample\ Volume}$$

Soil samples

Reagents

➤ General: The reagents used shall meet the purity requirements of the subsequent analysis. Their purity shall be verified by performing a blank test.

➤ Water: The water used shall comply with grade 2 of ISO 3696, or better.

Note: Deionizer water may be used, providing that it meets the requirements given above. It is recommended that the same batch of water is used throughout a given batch of dermination and those blank determinations are carried out.

➤ Hydrochloric acid, concentrated (HCl) = 12.0 mol/l

➤ Nitric acid, concentrated (HNO3,) = 15.8 mol/l

➤ Nitric acid, c (HNO₃) = 0.5 mol/l. Dilute 32 ml of nitric acid (4.4) with water (4.2) to 1 liter

Standard Stock Solution

➤ Manganese stock solution, 1000 mg/l or ppm manganese: Dissolve 3.076 g of manganese sulfate (MnSO₄.H₂O) in1 liter of 1 N HCl solution.

➤ Copper stock solution, 1000 mg/l or ppm Cu: Dissolve 3.929 g of Copper sulfate (CuSO₄ and 5H₂O) in a liter of 1 N HCl solution.

➤ Zinc stock solution, 1000 mg/l or ppm Zn: Dissolve 4.398 g of Zinc sulfate hepta hydrate (ZnSO4.7H2O) in about 500 ml distilled water in a 1000 ml volumetric flask. Add 10 ml of 5 M nitric acid and bring up to volume with distilled water.

➤ Cadmium: Dissolve 0.100 g cadmium metal in 4 ml concentration HNO₃. Add 8.0 ml concentration. HNO₃ and dilute to 1000 ml with water; 1.00 ml = 100 µg Cd

➤ Lead*:* Dissolve 0.1598 g lead nitrate, Pb (NO₃)₂, in a minimum amount of 1 + 1 HNO₃, add 10 ml concentration. HNO₃, and dilute to 1000 ml with water; 1.00 ml = 100 µg Pb.

➤ Nickel: Dissolve 0.1000 g nickel metal in 10 ml hot conc. HNO₃, cool, and dilute to 1000 ml with distilled water; 1.00 ml = 100 µg Ni.

➤ Lanthanum solution, 0.1 %: Dissolve 2.66 g of lanthanum chloride, LaCl₃. 7H₂O in some distilled water and makeup to 1liter with distilled water.

Note: used purchased from certified reference material as standard.

Apparatus

➤ Test sieve of aperture size 0.150 mm, e.g. test sieve with gauze cloth preferably made from plastics materials, e.g. nylon.

- Desiccators of nominal volume 2 liters.
- Reaction vessel of nominal volume 250 ml.
- Reflux condenser straight-through type, with a conical ground-glass joint.

Note: Water-cooled condensers with a minimum effective length of at least 200 mm have been found suitable.

The effective length is the internal surface which is in contact with the cooling water. The overall external length of such condenser is usually at least 365 mm. Absorption vessels, non-return type.

Note: the absorption vessel is only necessary when mercury is to be determined

Procedures

- First weigh 3gm of sample into the reaction vessel, moisten with 1.0 ml of water was added while mixed 21 ml HCl followed by 7 ml HNO_3 drop by drop.
- Then 15 ml dilute HNO_3 (0.5 mol/l) was added to the absorption vessel and connected with reaction vessel and allowed to stand for 16 hours at room temperature.
- Raised temperature until reflux conditions and maintained for 2 hours, then allowed to cooled, added contents of the absorption vessel to reaction vessel via a condenser, rinsed with further 10 ml dilute HNO_3 (0.5 mol/l), transferred relatively sediment free supernatant carefully through the filter and collected filtrate in a volumetric flask.
- Washed insoluble residue onto the filter paper with nitric acid, collected this filtrate with the first and the extract thus prepared was ready for the determination of elements by FAAS.
- Established the concentration/absorbance curve for the working standard solutions containing the lanthanum solution for each of the element by aspirating into the air-acetylene flame and measuring the absorbance or concentrations were undertaken at the following analytic respective wavelengths:
- Copper 324.7nm

- Cadmium 228.8nmLead 283.3nm
- Zinc 213.9nm
- Lead 283.3nm

Annex 3. Apparatus, Reagents and Procedures used for Biological and Chemical Parameters

Nitrate, sulfate, and fluoride were measured by spectrophotometer method based on pot lab + (C) XA Physical and chemical parameters test kit spectrophotometer (Plain test 7500, Wag Tech Company, UK model) through the following procedure.

- First taken a clean nitrate test tube (PT 526) then using the measuring syringe (PT 361)

- Added 1 ml of the sample then filled the nitrate test tube to the 20ml mark with deionized water.

- Added one level spoonful of nitrate test powder and one nitrate test tablet and did not crush the tablet then replaced screw cap and shacked tube well for exactly one minute and allowed contents to settle.

- Then inverted the tube gently 2 times and allowed to stand for at least two minutes to ensure complete settlement.

- Removed screw cap and wiped around top with a cleaned tissue then used the plain test filtration set to filtered a portion of solution through a GF/B filter paper into a test cuvette filled to the 10ml mark and added one nitricol tablet, crushed and mixed to dissolved the standee for 10 minutes, finally taken photometer for direct read the result in mg/l.

- Fluoride and sulfate were measured through the following procedures.

- First filled round test tube with the sample to the 10 ml mark

- then added one fluoride, and sulfate tablets separately,

- crushed and mixed to dissolve the standee for 10 minutes to the allowed full-color development

- selected spectrophotometer directly read the result in mg/l

BOD$_5$

Apparatus

- Incubation bottles (BOD Bottle):
- Burette
- Pipette, micro-pipette with dispenser.
- Bio-Chemical culture box.
- Beaker.
- Glass rod.

Reagents

- Phosphate buffer solution: Dissolve 42.5 gm potassium dihydrogen phosphate (KH_2PO_4) or 54.3g K_2HPO_4 in about 700 ml distilled water. Adjust pH to 7.2 with 30% sodium hydroxide (NaOH) and dilute to 1L. Alternatively Dissolve 8.5 g potassium dihydrogen phosphate (KH_2PO_4), 21.75 g dipotassium hydrogen phosphate (K_2HPO_4), 33.4 g disodium hydrogen phosphate heptahydrate ($Na_2HPO_4.7H_2O$) and 1.7 g ammonium chloride (NH_4Cl) in about 500 ml distilled water and dilute to 1 liter. The pH of this buffer should be 7.2 without further adjustment. Discard the reagent if there is any sign of biological growth in the stock bottle.

- Magnesium sulphate solution: Dissolve 22.5 g magnesium sulphate hepta hydrate ($MgSO_4.7H_2O$) in distilled water and dilute to 1 liter.

- Calcium chloride solution: Dissolve 27.5 g $CaCl_2$ in distilled water and dilute to 1 liter.

- Ferric chloride solution: Dissolve 0.25 g $FeCl_3.6H_2O$ in distilled water and dilute to 1 liter.

- Manganese sulfate solution: Dissolve 480 g $MnSO_4.4H_2O$, 400 g $MnSO_4.2H_2O$, or 364 g $MnSO_4.H_2O$ in distilled water, filter, and dilute to 1 L. The $MnSO_4$ solution

should not give a color with starch when added to an acidified potassium iodide (KI) solution.

➢ Alkali-iodide-azide reagent: Dissolve 125 g NaOH (or 175 g KOH) and 33.75 g NaI (or 37.5 g KI) in distilled water and dilute to 250 ml and Add 2.5 g NaN_3 dissolved in 10 ml. distilled water. Potassium and sodium salts may be used interchangeably. This reagent should not give a color with starch solution when diluted and acidified.

➢ Sulfuric acid, H_2SO_4, conc.: One milliliter is equivalent to about 3 mL alkali-iodide-azide reagent.

➢ Starch, 2%: Use either an aqueous solution or soluble starch powder mixtures. To prepare an aqueous solution, dissolve 2 g laboratory-grade soluble starch and 0.2 g salicylic acid, as a preservative, in 100 ml hot distilled water and boil.

➢ Standard sodium thiosulfate titrant: 0.025N: Dissolve 6.205 g $Na_2S_2O_3.5H_2O$ in distilled water. Add 1.5 ml 6N NaOH or 0.4 g solid NaOH and dilute to 1000 ml Standardize with Potassium dichromate ($K_2Cr_2O_7$) or bi-iodated solution $KH(IO_3)_2$.

➢ Standardization:—Dissolve approximately 2 g KI, free from iodated, in an Erlenmeyer flask with 100 to 150 ml distilled water. Add 1 ml 6N H_2SO_4 or a few drops of concentration. H_2SO_4 and 20ml of standard 0.025N $K_2Cr_2O_7$ or 20.00 ml standard bi-iodated solution. Dilute to 200 ml and titrate liberated iodine with thiosulfate titrant adding starch toward end of titration, when a pale straw color is reached. When the solutions are of equal strength, 20.00 ml 0.025N $Na_2S_2O_3$ should be required. If not adjust the $Na_2S_2O_3$ solution to 0.025N.

➢ Acid and alkali solution, 1N (H_2SO_4& NaOH): for neutralization of alkaline or acidic samples.

➢ Dilution water: Use distilled dematerialized, tap, or natural water for making sample dilutions.

➢ Preparation of dilution water: Place desired volume of water in a suitable water jug or bottle and add 1 ml each of phosphate buffer, $MgSO_4$, $CaCl_2$, and $FeCl_3$ solutions/L of water. Test dilution water quality by doing blank always is on hand. Before use bring dilution water temperature to $20 \pm 3°C$ preferably do not store prepared dilution water for more than 24 h after adding nutrients, minerals, and buffer.

Procedures

➢ The sample and dilution water (i.e. using water jug) were placing them into biochemical culture box about 20°c.

➢ Appropriately mixed the sample and checked pH of samples before it could be tested and it should become between 6.5 and 7.5 adjusted the sample by added sufficient amount of alkali (NaOH) or acid (H_2SO_4) to bring the sample within the range.

➢ Then 1ml each of phosphate buffer, magnesium sulfate solution, calcium chloride solution and ferric chloride solution for every liter of distilled water were added in order to prepare the dilution water.

➢ Saturate the dilution water in the flask by aerating.

➢ Since the source of the samples were leachate and river water stream taken at 25-100% dilution of the original samples before starting the analysis.

➢ Then added 20 ml of sample into a 300 ml incubation bottles (BOD bottle)

➢ Added the dilution water up to half of the neck.

➢ Then prepared blank by filling the BOD bottle with dilution water only for both DO_1 and DO_2.

➢ Determine the dissolved oxygen contents in the bottles using azide modification of the titrimetric iodometric method (Section 4500-O.C).

➢ Then determine the initial dissolved oxygen (DO_1) contents of the sample collected in a 300 ml BOD bottle by adding 1 ml $MnSO_4$ solution, followed by 1 ml alkali-iodide-azide reagent.

➢ Then stopper carefully to exclude air bubbles and mixed by inverting bottle a few times.

➢ When precipitate was settled sufficiently (to approximately half the bottle volume) to leave clear supernatant above the manganese hydroxide floc, add 1.0 ml concentration of H_2SO_4.

➢ Re stopper and mixed by inverting several times until dissolution was completed.

➢ Then Titrate with 0.025N $Na_2S_2O_3$ (sodium thiosulfate titrant) solution to a pale straw color and added a few drops of starch solution and continue titration to the

first disappearance of blue color to colorless or to the color of the prepared sample and recorded the volume (V_1).

➤ Place the set of bottles to be incubated in a BOD_5 incubator for 5 days at 20°C. Care should be taken to maintain the water seal over the bottles throughout the period of incubation.

➤ After 5 days incubation determines to dissolve oxygen in the samples using following steps help to measure dissolved oxygen initial note down the results (V_2).

➤ Finally, calculated the BOD_5 of the sample based on the following procedure:

$$F = \frac{N \ of \ Na_2S_2O_3}{0.025 \ N}$$

$$DO_1 \equiv V_1 \times F$$

$$DO_2 \equiv V_2 \times F$$

$$BOD \ 5 \ in \ mg \ / \ L \equiv (DO_1 - DO_2 - B) \times DF$$

Where:

DO_1 = Dissolved oxygen (DO) of the diluted sample immediately after preparation in mg/l.

DO_2= DO of the diluted sample after 5day incubation at 20°C in mg/l.

V_1 = volume of $Na_2S_2O_3$ consumed by the sample at the first day in ml.

V_2= volume of $Na_2S_2O_3$ consumed after five-day incubation in ml.

B=Blank dissolved oxygen (DO) in mg/l.

DF=Dilution factor (i.e. unit less)

COD

Apparatus

- Reflux apparatus
- Condenser
- Burettes
- Pipettes
- BUCHI COD Accessory with K-438 Digestion apparatus
- Volumetric flask, conical flask (500m)

Reagents

- Concentration of H_2SO_4, density 1.84 g/ml
- Silver sulfate-Sulphuric acid reagent: Dissolve10 gm silver sulfate (Ag_2SO_4) in 35 ml water. Add in portion 965 ml concentration of sulphuric acid. Allow one or two days for dissolution the dissolution is enhanced by stirring or shaking.
- Standard ferrous ammonium sulfate *(FAS) titrant*: 0.12N: Dissolve 47.0 g of ammonium iron (II) sulphate hexahydrate (($NH4)_2$ Fe ($SO4)_2.6H_2O$) in distilled water. Add 20 ml conc. Sulphuric acid (H_2SO_4). Cool and dilute with distilled water to1000ml. Standardize this reagent against the standard potassium dichromate ($K_2Cr_2O_7$) solution.
- Barium Diphenyl amine sulphonate indicator (BDS) $C_{24}H_{20}BaN_2O_6S_2$: Dissolve 1gm $C_{24}H_{20}BaN_2O_6S_2$ in 100 ml conc. H_2SO_4.
- Potassium dihydrogen phthalate (HOOCC6H4COOK):Dissolve0.170gm of potassium dihydrogen phthalate $KHC_8H_4O_4$, dried at 105^oC for 2h, in a distill water. Add 5ml concentration of sulphuric acid and dilute with water to 1000ml.this solution is stable for 1 week if stored at4^oC

Procedures

- Placed the preparation block into freezer or refrigerator and allowed cooling to avoid loss of volatile compounds while preparing the sample. Switched on the digester unit and program the parameters temperature 150^O_C and time 120 minutes preheat the digester to the required temperature.

➤ The standard 2 hours reflux time may be reduced if it has been shown that a shorter period yields the same results.

➤ Placed the rack on the cold preparation block and placed the digestion tubes in the rack, fixed the digestion tubes with the digestion tube holder.

➤ Transferred 15ml of the sample to the COD digestion tube, added 10 ml of the potassium dichromate solution and mixed well and added 25 ml of silver sulfate-sulphuric acid solution slowly. Immediately placed the condenser on the sample tubes and fixed them and placed the rack with the sample on the preheated digester.

➤ Then the digestion unit was reached the required temperature and showed "READY" press "START" and started the digestion process and allowed digesting for 120 minutes.

➤ After digestion cooled the tubes to about $60^{o}C$ and cleaned the condenser with a small volume of water.

➤ Disconnected reflux condenser and diluted the volume to at least 100ml with water or dilute the mixture to about twice its volume of distilled water and cooled it to room temperature.

➤ Then placed the rack including samples on the preparation block, removed the tube holder, transferred the containing solution to a 500 ml conical flask and added 2ml of Barium Diphenylamine sulphonate (BDS) indicator and titrate excess potassium dichromate ($K_2Cr_2O_{7)}$ with standard ferrous ammonium sulfate.

➤ Control Sample: Use 20 ml of potassium dihydrogen phthalate solution instead of sample and perform the procedure given above. The theoretical oxygen demand of this solution is 200 mg/l. The procedure was satisfactory while the result was between 192 and 208 mg/l. Then calculate the result in the following procedure;

$$COD \quad as \ mg \ of \ O2/L = \frac{(Vb - Vs) \times N \times 8000}{ml \ of \ sample}$$

Where:

N= concentration of ferrous ammonium sulfate.

8000= mill equivalent weight of oxygen × 1000 ml/l.

V_b= ml of ferrous used for blank

V_s= ml of ferrous used sample (APHA, 1999).